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(IZVESTIYA AKADEMY NAUK SSSR)

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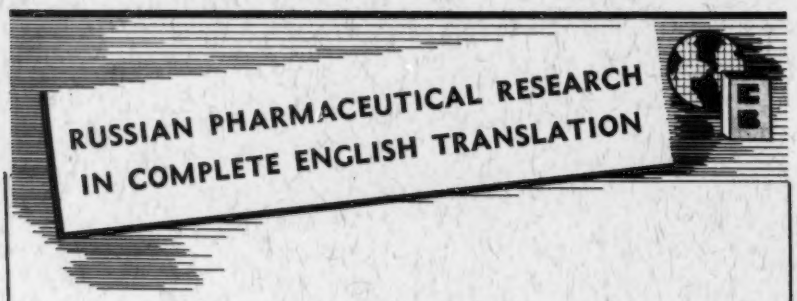

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 12. THE TERNARY SYSTEM $Zn(OH)_2$–H_2O_2–H_2O

S. Z. Makarov and L. V. Ladeinova

The great majority of the methods of preparing zinc peroxide are associated with the use of zinc hydroxide and hydrogen peroxide. However, the reactions between these substances cannot be regarded as simple, for numerous compounds are formed, the composition and nature of which have still not been adequately elucidated. Zinc peroxide was first prepared by Thenard in 1818 by dissolution of zinc oxide in a cold mixture of HCl and H_2O_2 and treatment of the resulting solution with caustic alkali [1]. In a later investigation the same worker obtained a zinc peroxide of composition Zn_2O_3 by the action of aqueous H_2O_2 solutions on $Zn(OH)_2$ [2].

The numerous investigations on zinc peroxide carried out from 1818 right up to the present day may be divided into several groups according to the character of the peroxides obtained and the way in which their compositions were interpreted. The first group includes those investigations in which the compounds obtained are regarded as pure peroxides: Thenard [2] – Zn_2O_3; Haass [3] – Zn_5O_8 and Zn_3O_5; and Ebler [4] – Zn_2O_5. Another group of investigators regards the peroxy compounds of zinc as chemical compounds of zinc peroxide with zinc hydroxide: Kurilov [5, 6] – $ZnO_2 \cdot Zn(OH)_2$; and Eijkman [7] – $3ZnO_2 \cdot Zn(OH)_2$. In most of the papers zinc peroxide compounds are considered to be of the hydrate type: Kazanetsky [8] – $3ZnO_2 \cdot 3H_2O$; Ebler and Krause [9] – $ZnO_2 \cdot 0.5H_2O$; Carrasco [10] – $Zn_4O_7 \cdot 2H_2O$ and $Zn_3O_5 \cdot H_2O$; Riesenfeld and Nottebohm [11] – $ZnO_2 \cdot 0.5H_2O$; Gogne [12] – $ZnO_2 \cdot 0.5H_2O$; and Pierron [13] – $ZnO_2 \cdot H_2O$, $Zn_2O_3 \cdot H_2O$ and $Zn_3O_5 \cdot H_2O$. Teletov [14] gives a more complex formula: $10ZnO_2 \cdot 4ZnO \cdot 5H_2O$ and $8ZnO_2 \cdot 4ZnO \cdot 7H_2O$. DeForcrand [15, 16] regards peroxy compounds of zinc as anhydrous or hydrated forms of zinc peroxide with combined hydrogen peroxide, i.e. as a perhydrate or, more exactly, hydrate-perhydrate type: $Zn_3O_3 \cdot 2H_2O_2$, $Zn_4O_4 \cdot H_2O \cdot 3H_2O_2$, $ZnO \cdot H_2O \cdot H_2O_2$, $Zn_3O_3 \cdot H_2O \cdot 2H_2O_2$. In later papers, published in 1917, 1946, and 1950, Sjostrom [17], Moles [18], and Pierron [19] propose a hydroperoxide structure for the zinc peroxide, e.g., $Zn(OOH) \cdot (OH)$.

Hence, with regard to the chemical compositions of the peroxy compounds of zinc the position is not sufficiently clear. If we try to fit the reported data in the phase diagram $ZnO - H_2O - O_{act}$ (Figure 1), some interesting points emerge. On the line $ZnO_2 - H_2O$ quite difinite positions are occupied by the figurative points $ZnO_2 \cdot 0.5H_2O$, $ZnO_2 \cdot H_2O$ and $ZnO_2 \cdot 2H_2O$, the probability of the correctness of these compositions being very high. The possibility of other compounds, such as $ZnO \cdot 0.5H_2O_2$ and $ZnO \cdot H_2O_2$ (or $ZnO_2 \cdot H_2O$), is not excluded, but the behavior of compounds of this type when heated points to the more complex nature of peroxy compounds of zinc, which gives grounds for regarding them as compounds of the hydroperoxide type.

In an investigation by Schechter and Kleinberg [20] in 1954, anhydrous zinc peroxide ZnO_2 was synthesized by an exchange reaction between $Zn(NO_3)_2$ and KO_2 in liquid ammonia, in accordance with the equation:

$$Zn(NO_3)_2 + 2KO_2 \rightarrow Zn(O_2)_2 + 2KNO_3 \rightarrow ZnO_2 + O_2 + 2KNO_3.$$

However, no data are given in confirmation of the actual composition of the zinc peroxide obtained.

The most remarkable feature of all the papers cited is the absence of any systematic investigation by methods of physicochemical analysis. It is probably the extensive use of preparative methods of synthesis

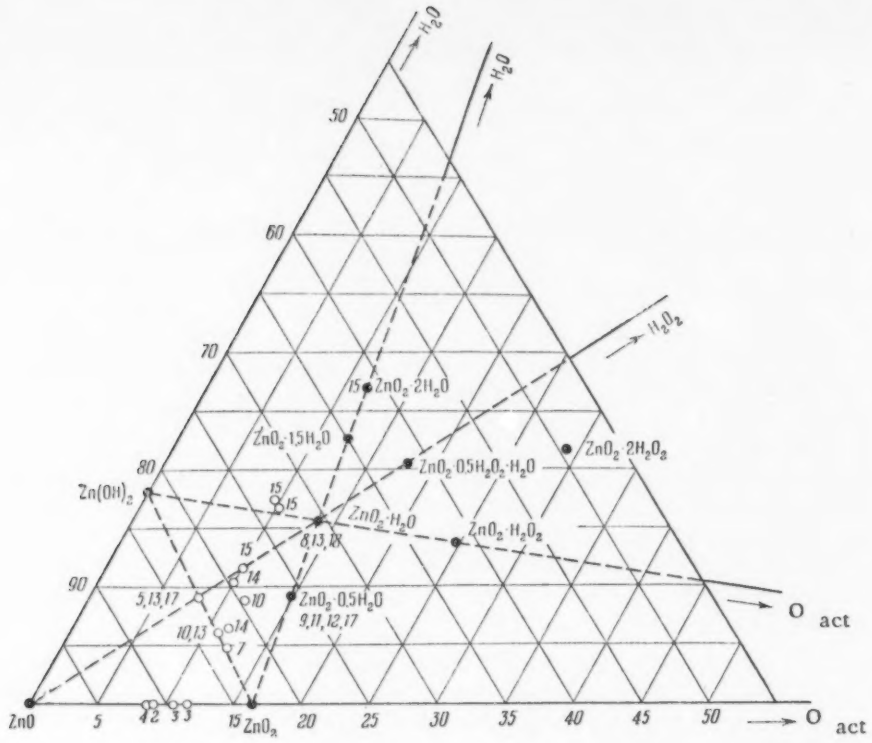

Fig. 1. O) experimental data; ●) data from literature

that has led to such a great variety of compositions attributed to zinc peroxides. The diagram (Figure 1) gives some grounds for the view that many of the compounds described in the literature may be regarded as mechanical mixtures of two or three compounds in the region of the diagram $ZnO - Zn(OH)_2 - ZnO_2 \cdot H_2O - ZnO_2$. In view of the obscurity that exists about the peroxy compounds of zinc— the most typical member of the subgroup of Group II of the periodic system – we began a study of the peroxy compounds of zinc, considered as phases in the system $Zn(OH)_2 - H_2O_2 - H_2O$.

EXPERIMENTAL

1. Procedure

The system $Zn(OH)_2 - H_2O_2 - H_2O$ was investigated by the solubility method. We used pure zinc hydroxide, prepared from zinc nitrate and ammonia solutions, and hydrogen peroxide freed from impurities and stabilizers by vacuum distillation. The thermostat consisted of a 500-ml Dewar vessel mounted in asbestos in a 12-liter Dewar vessel. In the experiments, constancy of temperature was maintained within ±0.5°. For 0° the smaller vessel contained ground ice, for − 10° it contained a mixture of KCl and ice, and for − 20° it contained a mixture of NaCl and ice.

Before the experiment, the zinc hydroxide and hydrogen peroxide solutions were cooled to the necessary temperature, and the zinc hydroxide was then stirred with the hydrogen peroxide in the usual solubility vessels for a definite period of time, determined beforehand as that necessary for the attainment of equilibrium (constancy of active-oxygen content in the liquid and solid phases). It was shown that at 0, − 10, and − 20° it was necessary to stir for two hours, whereas at 20 and 30° 90 minutes was sufficient. Test samples were taken with an apparatus consisting of a No. 3 sintered glass funnel and a test tube with side tube for the liquid phase. This apparatus was also thermostated in a Dewar vessel. The residue and liquid phase were analyzed for active-oxygen and zinc oxide contents. Active oxygen was determined by titration with 0.1 N $KMnO_4$ in presence of

H_2SO_4. Zinc oxide was determined in the residue in the form of zinc ammonium phosphate, which was calcined to zinc pyrophosphate. Owing to low solubility, the zinc oxide content of the liquid phase was determined colorimetrically [21] with dithizone with the aid of an FEK-2 photoelectric colorimeter.

2. Data for the Solubility Isotherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

The ternary system $Zn(OH)_2 - H_2O_2 - H_2O$ was studied in the temperature range from 30° down to − 20°, isotherms being determined at 30, 20, 0, − 10, and − 20°.

It should be noted that some of the radial ties drawn through figurative points in accordance with the analytical results do not converge with adequate precision on the point representing the composition of the solid phase on the diagram. Some of these discrepancies are due to partial decomposition of the residue or liquid phase. In order to reduce possible errors in the determination of the true compositions of solid phases, supplementary $ZnO - H_2O_2$ diagrams were used in the liquid phase, because these determine the number and existence limits of each solid phase of the system with greater reliability. The composition at transition points was found mainly from the position of maxima on the solubility curve of the $ZnO - H_2O_2$ diagram.

TABLE 1

Solid Phases of the System at 30°

Solid phase	Lower limit (% H_2O_2)	Upper limit (% H_2O_2)
$Zn(OH)_2$	0.00	1.92
$ZnO_2 \cdot 2H_2O$	1.92	15.68
$ZnO_2 \cdot 1.5H_2O$	15.68	41.40
$ZnO_2 \cdot H_2O$	41.40	58.33
$ZnO_2 \cdot 0.5H_2O$	58.33	82.52
ZnO_2 (unstable)	82.52	>93.23

The 30° isotherm was studied from 0.00 to 93.23% of H_2O_2 in the liquid phase.

As will be seen from the diagram in the triangular system of coordinates (Figure 2) and from the solubility curve (Figure 3), we may assume the presence of six solid phases at 30° over this range of H_2O_2 concentrations (Tables 1 and 2).

At positive temperatures the solid phases are well formed and can be separated from the mother liquid with comparative ease.

The 20° isotherm was studied from 0.00 to 88.68% of H_2O_2 in the liquid phase. The results are given in Tables 3 and 4 and the graphs of Figures 4 and 5. We may assume the existence of six solid phases at 20°.

The 0° isotherm was studied from 0.00 to 90.15% of H_2O_2 in the liquid phase. Results of the systematic investigation of the 0° isotherm are given in Tables 5 and 6 and in the graphs in Figures 6 and 7.

The − 10° isotherm was studied from 16.00 to 90.00% of H_2O_2 in the liquid phase. Outside these limits hydrogen peroxide solutions freeze. The results on the system at − 10° are given in Tables 7 and 8 and in the graphs of Figures 8 and 9.

The composition of the solid phase of the first branch of the isotherm (Figure 8) cannot be determined exactly graphically by the method of "residues," since the tie uniting the figurative points of the liquid phase and the residue for Experiment 1 intersects the line of the compositions ZnO_2, $ZnO_2 \cdot 0.5H_2O$, $ZnO_2 \cdot H_2O$ at an acute angle. The solid phase $ZnO_2 \cdot H_2O$ was therefore taken as the limiting possibility, the data of Figure 9 being taken into account. In the region of H_2O_2 concentrations from 13.80 to 20.43%, which are close to their freezing points, the liquid phases are characterized by high viscosity, which makes it difficult to take samples for investigation.

The − 20° isotherm was studied from 26.00 to 83.00% of H_2O_2 in the liquid phase, since weaker and more concentrated solutions freeze. The results are given in Tables 9 and 10 and in the graphs of Figures 10 and 11.

The composition of the first solid phase at − 20°, as established from the data in Figures 9 and 10, taken as a whole, may be taken as $ZnO_2 \cdot 0.5H_2O$.

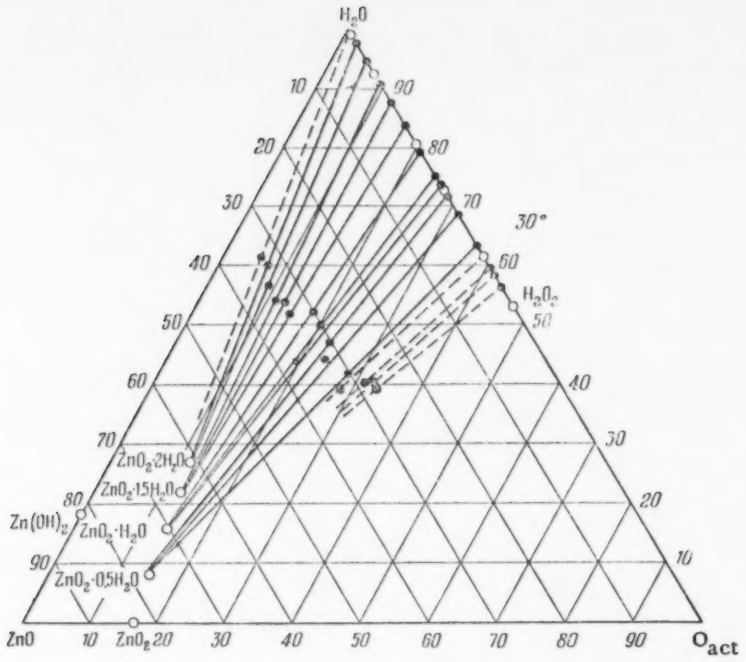

Fig. 2.

TABLE 2

The 30° Isotherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

Experiment	Composition of residue (% by weight)		Composition of liquid phase (%)			Solid phase
	O_{act}	ZnO	O_{act}	H_2O_2	$ZnO \cdot 10^{-4}$	
28	—	—	—	—	1.03	$Zn(OH)_2$
1	6.07	32.94	0.90	1.92	6.08	$Zn(OH)_2 + ZnO_2 \cdot 2H_2O$
2	7.73	32.37	2.95	6.27	4.28	$ZnO_2 \cdot 2H_2O$
15	—	—	3.95	8.45	8.13	Ditto
3	9.42	34.16	5.56	11.83	10.68	" "
22	—	—	6.31	13.43	12.10	" "
11	10.81	32.65	7.38	15.68	24.30	$ZnO_2 \cdot 2H_2O + ZnO_2 \cdot 1{,}5H_2O$
9	11.83	34.25	9.36	19.89	12.18	$ZnO_2 \cdot 1.5H_2O$
7	12.86	33.45	12.25	26.09	9.42	Ditto
4	14.84	33.59	16.28	34.60	4.68	" "
29	—	—	19.16	40.74	8.90	
31	—	—	—	—	—	$ZnO_2 \cdot 1{,}5H_2O + ZnO_2 \cdot H_2O$
32	—	—	19.92	42.18	8.93	$ZnO_2 \cdot H_2O$
25	—	—	20.21	43.00	5.70	Ditto
10	18.06	29.90	20.80	44.18	4.10	" "
26	20.20	30.02	25.35	53.65	—	" "
17	21.94	—	26.01	55.27	1.15	" "
13	—	—	26.20	55.77	4.25	" "
5	19.59	36.10	26.89	57.16	14.25	" "
33	—	—	27.46	58.33	22.58	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0{,}5H_2O$
12	22.82	30.00	28.81	62.25	5.57	$ZnO_2 \cdot 0.5H_2O$
8	23.39	32.66	31.74	67.51	2.43	Ditto
14	28.09	29.99	36.92	78.61	0.78	" "
6	27.90	32.50	38.53	82.52	1.98	$ZnO_2 \cdot 0{,}5H_2O + ZnO_2$
27	—	—	40.09	85.31	0.77	ZnO_2 (unstable)
18	31.56	28.49	40.89	86.98	0.75	Ditto
20	32.37	27.34	41.61	88.45	0.53	" "
21	34.70	27.45	43.80	93.23	0.78	

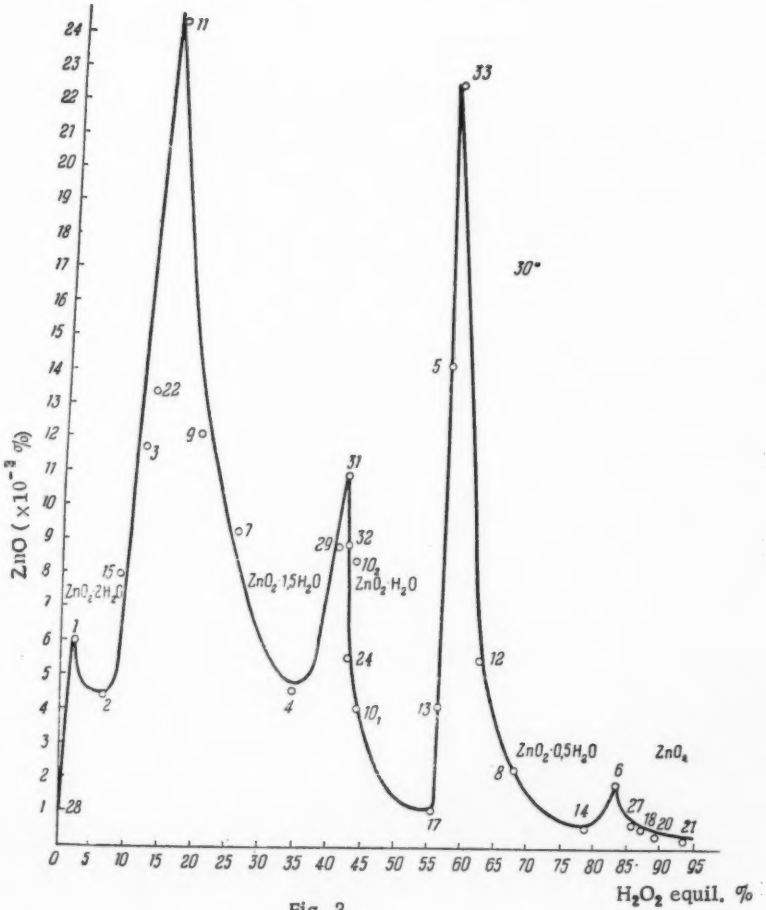
ZnO (×10⁻³ %)
H₂O₂ equil. %
30°
ZnO₂·2H₂O
ZnO₂·1,5H₂O
ZnO₂·H₂O
ZnO₂·0,5H₂O
ZnO₂

Fig. 3.

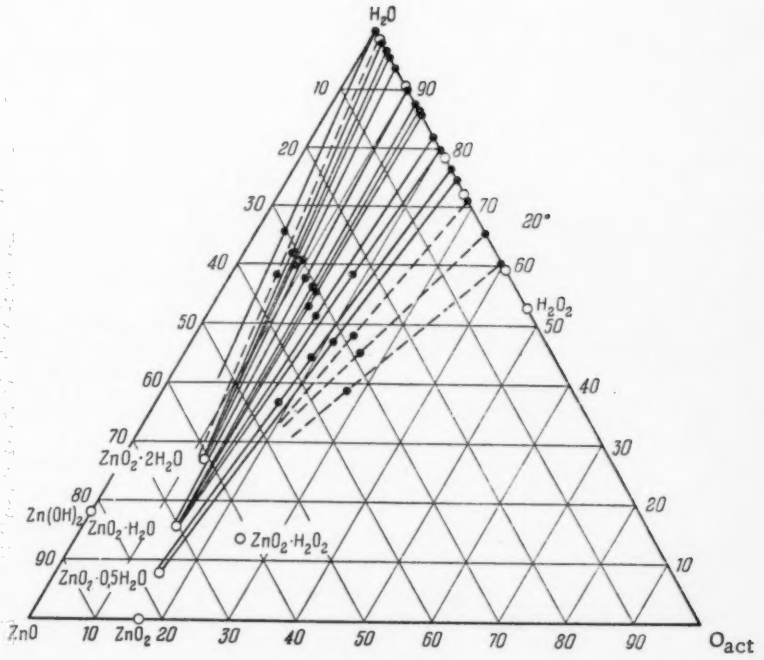
H₂O
H₂O₂
20°
ZnO₂·2H₂O
Zn(OH)₂
ZnO₂·H₂O
ZnO₂·H₂O₂
ZnO₂·0,5H₂O
ZnO
ZnO₂
Oact

Fig. 4.

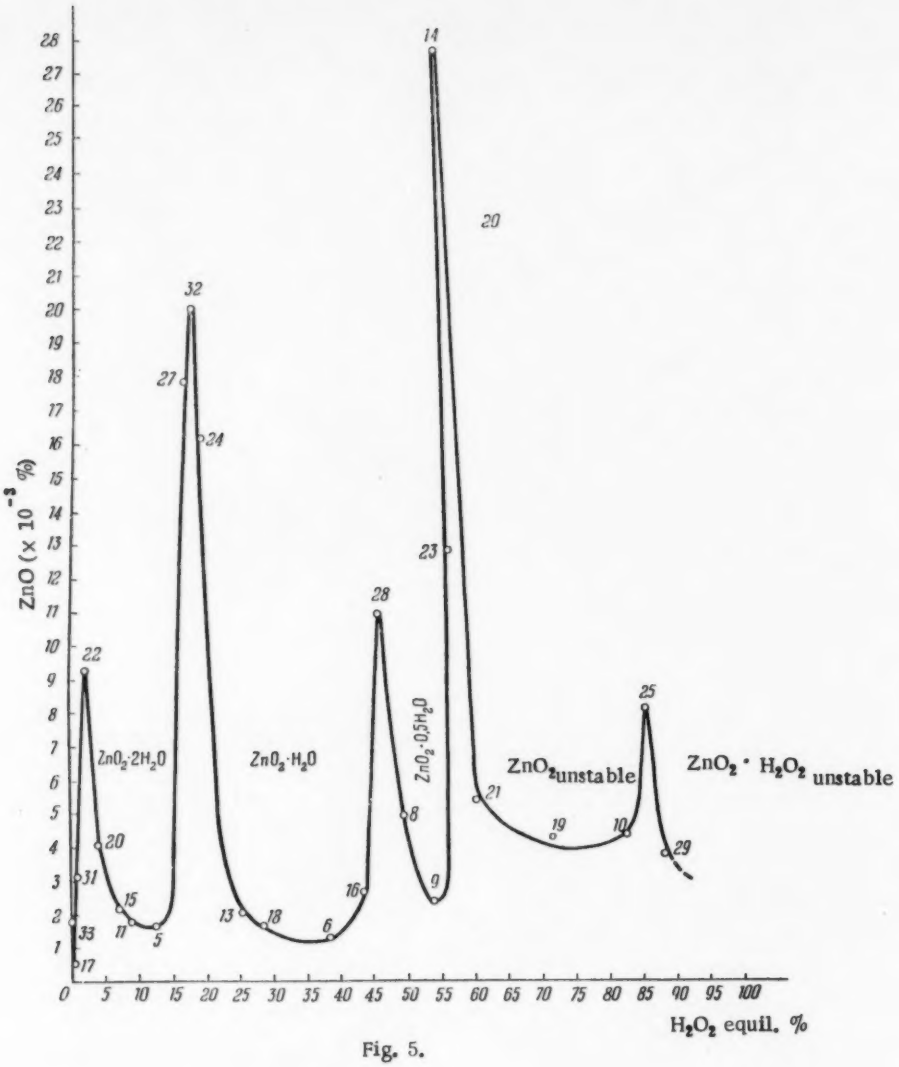

Fig. 5.

TABLE 3

Solid Phases of the System at 20°

Solid phase	Lower limit (% H_2O_2)	Upper limit (% H_2O_2)
$Zn\cdot(OH)_2$	0.00	3.48
$ZnO_2\cdot 2H_2O$	3.48	19.00
$ZnO_2\cdot H_2O$	19.00	46.54
$ZnO_2\cdot 0.5H_2O$	46.54	57.98
ZnO_2 (unstable)	57.98	86.15
$ZnO_2\cdot H_2O_2$ (unstable)	86.15	>88.68

TABLE 4

The 20° Isotherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

Experiment	Composition of residue (% by weight)		Composition of liquid phase			Solid phase
	O_{act}	ZnO	O_{act}	H_2O_2	$ZnO \cdot 10^{-4}$	
33	—	—	—	—	1.80	$Zn(OH)_2$
17	4.80	29.08	0.21	0.45	0.52	Ditto
31	—	—	0.79	1.67	3.13	" "
22	7.11	34.99	1.64	3.48	9.30	$Zn(OH)_2 + ZnO_2 \cdot 2H_2O$
20	7.23	30.67	2.22	4.72	4.18	$ZnO_2 \cdot 2H_2O$
15	8.03	30.10	3.56	7.62	2.19	Ditto
11	8.69	31.11	4.34	9.23	1.87	" "
5	9.70	29.89	6.09	12.94	1.72	" "
27	—	—	8.56	18.19	17.86	" "
32	—	—	—	~19.00	~20.00	$ZnO_2 \cdot 2H_2O + ZnO_2 \cdot H_2O$
24	11.26	31.10	10.07	21.43	16.23	$ZnO_2 \cdot H_2O$
13	13.84	30.52	12.24	26.04	2.14	Ditto
18	14.36	30.32	13.27	28.20	1.62	" "
7	14.12	32.55	14.87	31.64	—	" "
6	16.43	32.05	18.01	38.30	1.13	" "
16	18.73	23.22	20.65	43.86	2.53	" "
28	—	—	21.88	46.54	10.94	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0{,}5H_2O$
8	19.68	36.13	23.83	50.66	4.29	$ZnO_2 \cdot 0.5H_2O$
9	21.85	31.43	25.41	54.00	2.37	Ditto
23	20.69	—	27.20	57.50	12.90	" "
14	22.80	26.91	27.33	57.98	27.78	$ZnO_2 \cdot 0.5H_2O + ZnO_2$
21	23.66	27.78	28.38	60.29	5.42	ZnO_2 (unstable)
19	26.81	28.40	34.06	72.35	4.23	Ditto
10	28.06	33.77	39.09	83.07	4.44	" "
25	—	—	40.56	86.15	8.31	$ZnO_2 + ZnO_2 \cdot H_2O_2$
29	—	—	41.75	88.68	3.84	$ZnO_2 \cdot H_2O_2$ (unstable)

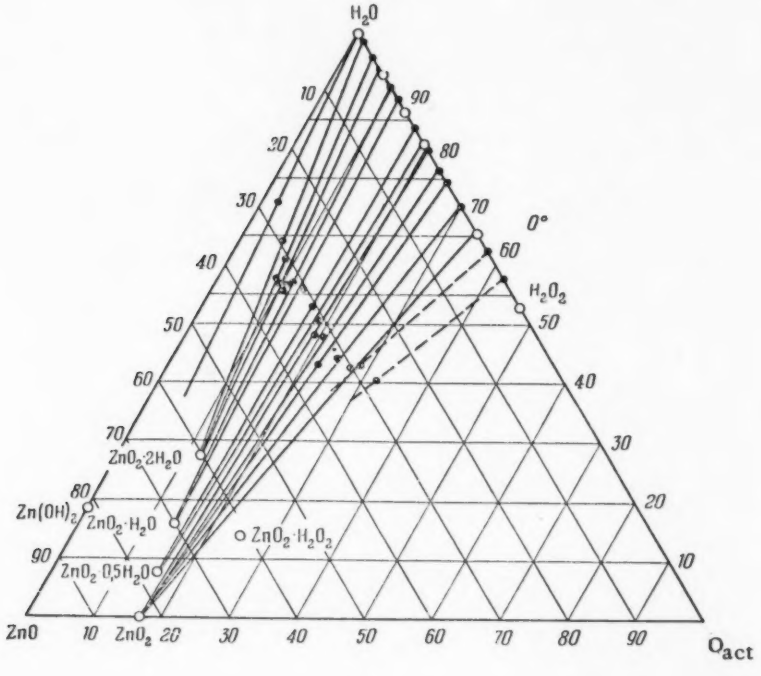

Fig. 6.

TABLE 5

Solid Phases of the System at 0°

Solid phase	Lower limit (% H_2O_2)	Upper limit (% H_2O_2)
$Zn(OH)_2$	0.00	0.07
$ZnO_2 \cdot 2H_2O$	0.07	15.09
$ZnO_2 \cdot H_2O$	15.09	28.34
$ZnO_2 \cdot 0{,}5H_2O$	28.34	40.93
ZnO_2	40.93	74.38
$ZnO_2 \cdot H_2O_2$ (unstable)	74.38	>90.15

TABLE 7

Solid Phases of the System at −10°

Solid phase	Lower limit (% H_2O_2)	Upper limit (% H_2O_2)
$Zn_2O \cdot H_2O$	<13.80	20.43
$ZnO_2 \cdot 0.5H_2O$	20.43	38.69
$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$	38.69	62.32
ZnO_2	62.32	72.65
$ZnO_2 \cdot H_2O_2$ (unstable)	72.65	>89.18

TABLE 6

The 0° Isotherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

Experiment	Composition of residue (% by weight)		Composition of liquid phase (%)			Solid phase
	O_{act}	ZnO	O_{act}	H_2O_2	$ZnO \cdot 10^{-3}$	
41	—	—	—	—	0.63	$Zn(OH)_2$
32	2.51	26.68	0.04	0.07	0.74	$Zn(OH)_2 + ZnO_2 \cdot 2H_2O$
31	6.78	29.36	1.61	3.50	0.44	$ZnO_2 \cdot 2H_2O$
5	8.99	33.84	2.94	6.25	0.39	Ditto
14	8.70	30.96	4.27	9.08	1.43	" "
16	9.04	33.73	4.37	9.29	—	" "
4	10.67	33.38	4.86	10.36	3.42	" "
35	—	—	6.10	13.96	3.66	" "
9	10.75	32.28	7.10	15.09	9.01	$ZnO_2 \cdot 2H_2O + ZnO_2 \cdot H_2O$
11	11.32	31.74	9.14	19.42	5.77	$ZnO_2 \cdot H_2O$
18	13.39	30.77	11.21	23.83	1.11	Ditto
39	—	—	12.78	27.16	2.36	" "
36	—	—	13.23	28.34	5.23	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0.5H_2O$
40	—	—	15.11	32.10	1.65	$ZnO_2 \cdot 0.5H_2O$
17	16.29	30.59	16.34	34.74	1.29	Ditto
3	18.40	30.52	18.92	40.24	4.29	" "
37	—	—	19.37	40.93	5.00	$ZnO_2 \cdot 0.5H_2O + ZnO_2$
19	19.07	32.43	20.53	43.65	1.98	ZnO_2
38	—	—	20.61	43.81	0.63	Ditto
21	20.73	31.38	23.88	50.77	1.06	" "
27	22.37	34.42	25.72	54.83	0.86	" "
20	24.63	31.24	29.90	63.77	1.29	" "
34	27.38	30.64	34.72	73.82	2.01	" "
30	—	—	34.98	74.38	19.72	$ZnO_2 + ZnO_2 \cdot H_2O_2$
22	28.22	28.62	37.55	79.83	7.76	$ZnO_2 \cdot H_2O_2$ (unstable)
28	32.38	27.36	42.34	90.15	1.05	Ditto

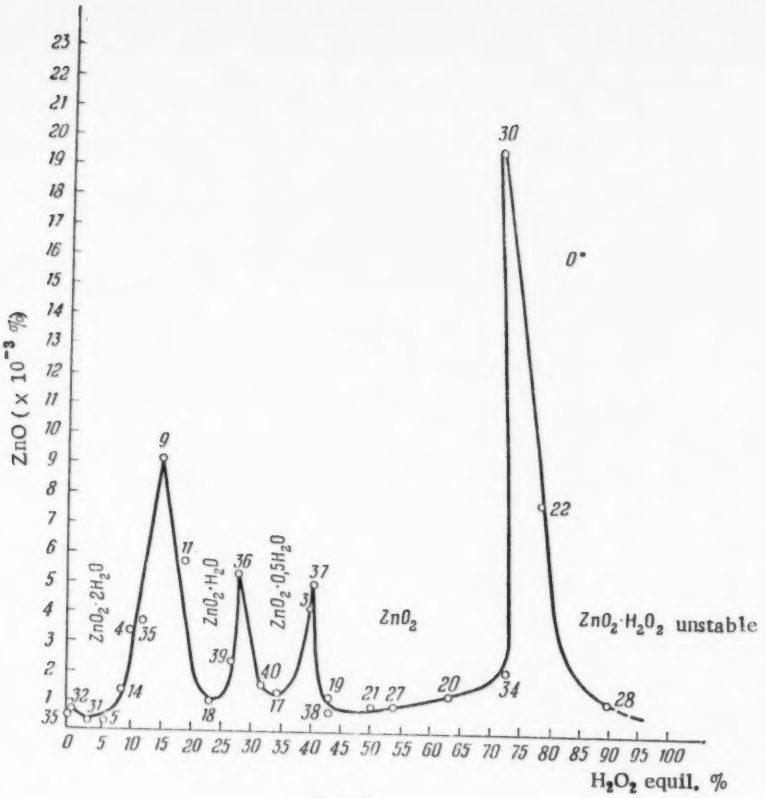
ZnO (× 10⁻³ %)
H₂O₂ equil. %
0°
ZnO₂·2H₂O
ZnO₂·H₂O
ZnO₂·0,5H₂O
ZnO₂
ZnO₂·H₂O₂ unstable

Fig. 7.

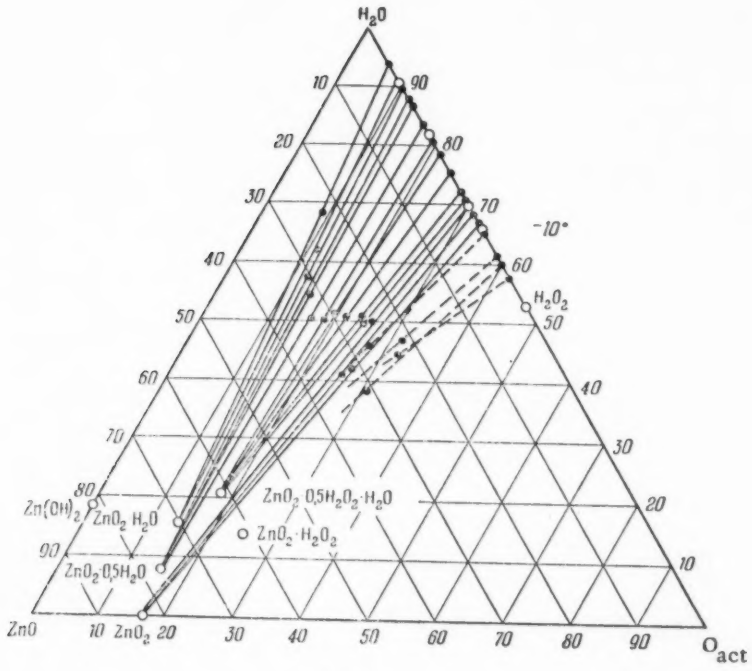
H₂O
-10°
H₂O₂
Zn(OH)₂
ZnO₂·H₂O
ZnO₂·0,5H₂O
ZnO₂·0,5H₂O₂·H₂O
ZnO₂·H₂O₂
ZnO
ZnO₂
Oact

Fig. 8.

TABLE 8

The $-10°$ Isotherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

Experiment	Composition of residue (% by weight)		Composition of liquid phase (%)			Solid phase
	O_{act}	ZnO	O_{act}	H_2O_2	$ZnO \cdot 10^{-3}$	
1	9.31	22.51	6.50	13.80	3.89	$ZnO_2 \cdot H_2O$
5	11.43	26.89	8.96	19.04	3.30	Ditto
21	—	—	9.60	20.43	4.37	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0.5H_2O$
25	—	—	10.14	21.54	3.22	$ZnO_2 \cdot 0.5H_2O$
15	12.66	30.18	10.55	22.43	2.75	Ditto
13	13.74	31.81	12.17	25.72	—	" "
2	14.75	31.32	13.33	28.30	2.16	" "
7	16.42	33.02	16.57	35.21	3.84	" "
30	—	—	16.66	35.48	4.80	" "
35	—	—	17.12	36.37	5.30	" "
34	—	—	18.00	38.69	6.61	$ZnO_2 \cdot 0.5H_2O + ZnO_2 \cdot 0,5H_2O_2 \cdot H_2O$
36	—	—	19.15	40.67	4.10	$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$
11	18.38	31.18	19.59	41.62	2.60	Ditto
31	—	—	21.25	45.22	2.10	" "
3	19.42	29.12	21.59	45.66	—	" "
6	—	—	23.89	50.74	1.49	" "
4	—	—	24.31	51.62	1.23	" "
14	21.48	27.33	24.71	52.43	1.12	" "
32	—	—	27.55	58.51	0.91	" "
9	23.57	25.77	27.70	58.85	—	" "
28	—	—	28.80	61.38	1.87	" "
27	—	—	29.10	61.89	1.86	" "
16	24.37	26.88	29.18	61.93	2.05	" "
19	23.93	27.48	29.34	62.32	8.03	$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O + ZnO_2$
29	25.52	24.49	30.16	64.41	1.40	ZnO_2
12	25.79	33.67	31.44	66.68	0.62	Ditto
17	26.43	31.12	33.36	70.83	1.84	" "
33	—	—	34.20	72.65	2.30	$ZnO_2 + ZnO_2 \cdot H_2O_2$
24	27.15	27.13	34.31	72.90	1.55	$ZnO_2 \cdot H_2O_2$ (unstable)
23	—	—	35.54	75.52	1.12	Ditto
20	31.92	21.49	38.53	80.48	1.41	" "
18	30.58	31.06	40.16	85.32	1.20	" "
10	32.24	23.15	42.02	89.18	0.77	" "

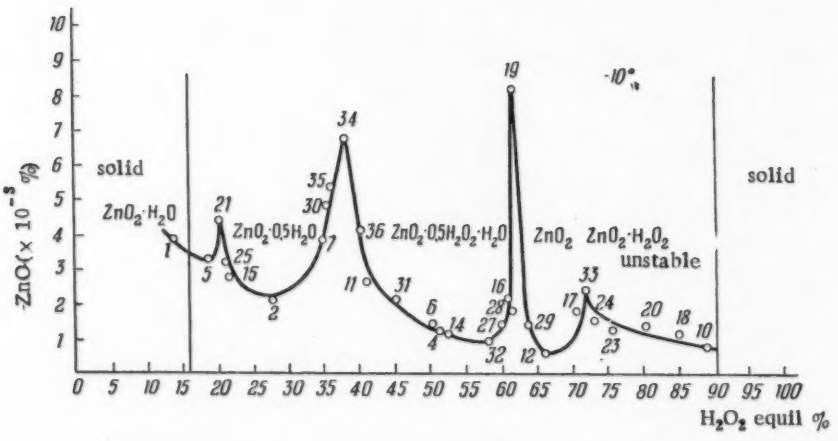

Fig. 9.

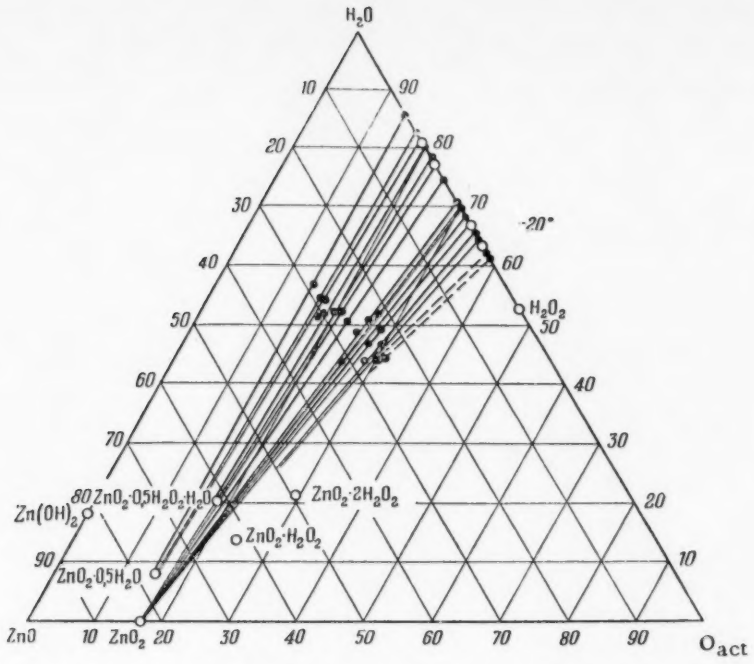

Fig. 10.

TABLE 9

Solid Phases of the System at − 20°

Solid phase	Lower limit (% H_2O_2)	Upper limit (% H_2O_2)
$ZnO_2 \cdot 0.5H_2O$	<30.00	40.23
$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$	40.23	48.03
ZnO_2	48.03	70.78
$ZnO_2 \cdot H_2O_2$ (unstable)	70.78	77.55
$ZnO_2 \cdot 2H_2O_2$ (unstable)	77.55	>81.66

3. Solubility Polytherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

As a result of the study of the 30, 20, 0, − 10, and − 20° isotherms, we determined the compositions at various transition points corresponding to the existence of two solid phases under equilibrium conditions. The data on the compositions of the liquid phases at the transition points are collected in Table 11 and are plotted on a diagram in rectangular coordinates (Figure 12) with temperature as ordinates, and the H_2O_2 content of the liquid phase (% by weight) as abscissas. The polythermal diagram defines the positions of 11 fields corresponding to the conditions for the existence of the solid phases: ice; hydrogen peroxide; $ZnO_2 \cdot 2H_2O$; $ZnO_2 \cdot 1.5H_2O$; $ZnO_2 \cdot H_2O$; $ZnO_2 \cdot 0.5H_2O$; ZnO_2; $ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$; $ZnO_2 \cdot H_2O_2$; and $ZnO_2 \cdot 2H_2O_2$.

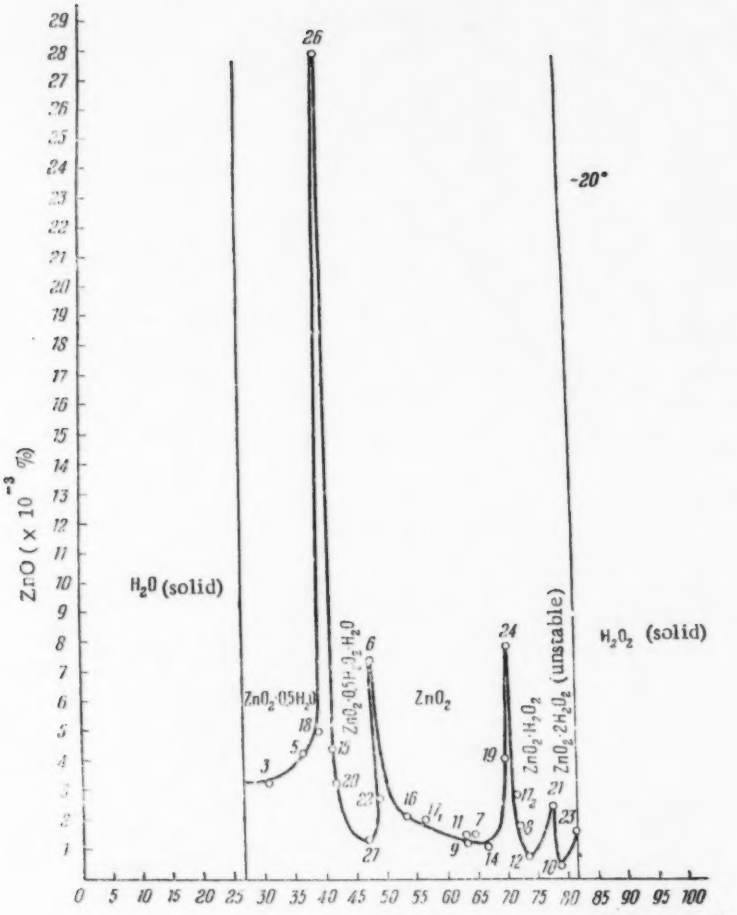
ZnO (× 10⁻³ %)
H₂O (solid)
ZnO₂·0.5H₂O
ZnO₂·0.5H₂O₂·H₂O
ZnO₂
ZnO₂·H₂O₂
ZnO₂·2H₂O₂ (unstable)
H₂O₂ (solid)
-20°
H₂O₂ equil. %

Fig. 11.

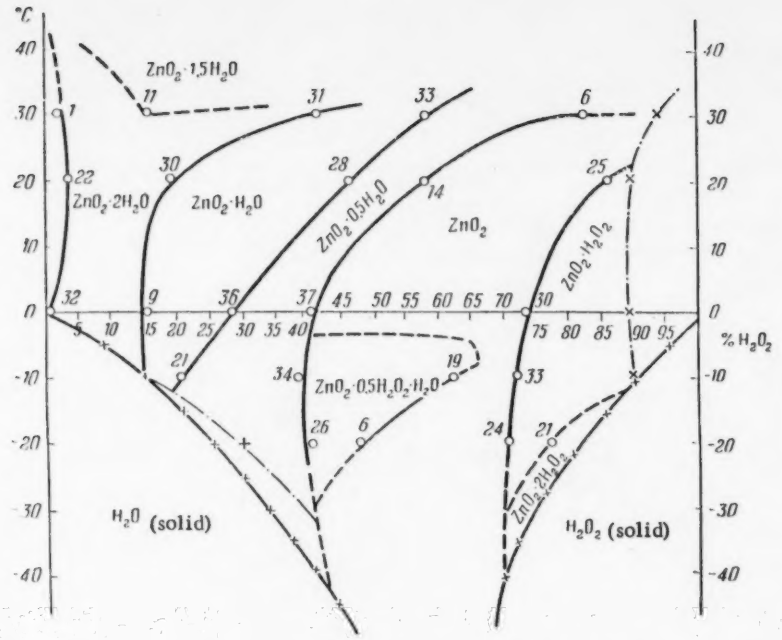

Fig. 12. —— definite limit of field; – – – indefinite limit of field; –·–·– limit within which system studied; –×–×– limits of ice and solid H_2O_2 fields.

TABLE 10

The – 20° Isotherm of the Ternary System $Zn(OH)_2 - H_2O_2 - H_2O$

Experiment	Composition of residue (% by weight)		Composition of liquid phase (%)			Solid phase
	O_{act}	ZnO	O_{act}	H_2O_2	$ZnO \cdot 10^{-3}$	
3	14.90	28.15	14.16	30.09	3.37	$ZnO_2 \cdot 0.5H_2O$
5	17.17	28.45	17.35	36.87	4.32	Ditto
18	17.88	28.78	18.30	38.96	4.99	" "
26	17.88	30.64	18.92	40.23	27.80	$ZnO_2 \cdot 0.5H_2O + ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$
15	18.81	32.31	19.53	41.51	4.03	$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$
20	18.86	29.03	19.64	41.74	3.29	Ditto
13	20.12	27.44	21.81	46.45	—	" "
27	—	—	22.35	47.52	1.33	" "
6	20.99	26.54	22.60	48.03	7.44	$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O + ZnO_2$
22	21.08	27.44	22.95	48.78	2.79	ZnO_2
16	22.77	26.95	25.43	54.02	2.02	Ditto
17	—	—	26.71	56.76	2.13	" "
11	25.82	23.21	29.69	63.43	1.50	" "
9	26.33	21.31	29.84	63.47	1.36	" "
7	24.63	30.87	30.38	64.47	1.65	" "
14	19.78	26.14	31.35	66.63	1.20	" "
19	27.55	25.37	32.89	69.86	4.07	" "
24	28.18	27.47	33.30	70.78	7.82	$ZnO_2 + ZnO_2 \cdot H_2O_2$
17	27.26	26.07	33.35	71.63	2.98	$ZnO_2 \cdot H_2O_2$ (unstable)
8	30.91	30.48	33.74	71.71	1.88	Ditto
12	29.82	23.77	34.50	73.31	0.84	" "
28	28.61	27.82	34.58	73.53	—	" "
25	29.41	25.76	35.87	76.25	1.48	" "
21	29.66	26.08	36.49	77.55	2.53	$ZnO_2 \cdot H_2O_2 + ZnO_2 \cdot 2H_2O_2$
10	30.01	25.55	37.28	79.23	0.52	$ZnO_2 \cdot 2H_2O_2$ (unstable)
23	31.43	24.54	38.27	81.66	1.62	Ditto

TABLE 11

Data on the Composition of the Liquid Phases for Transition Points of the Isotherms of the Ternary System

Temp. of transition point (°C)	Experiment corresponding to the transition point	Concentration in liquid phase: H_2O_2 (equilibrium) (%)	Concentration in liquid phase: ZnO ($\times 10^{-3}$ %)	Solid phase
+30	1	1.92	6.08	$Zn(OH)_2 + ZnO_2 \cdot 2H_2O$
	11	15.68	24.30	$ZnO_2 \cdot 2H_2O + ZnO_2 \cdot 1.5H_2O$
	31	21.40	~11.00	$ZnO_2 \cdot 1.5H_2O + ZnO_2 \cdot H_2O$
	33	58.33	22.58	$ZnO_2 \cdot H_2O + ZnO \cdot 0.5H_2O$
	6	82.52	1.98	$ZnO_2 \cdot 0.5H_2 \cdot O + ZnO_2$
+20	22	3.48	9.30	$Zn(OH)_2 + ZnO_2 \cdot 2H_2O$
	32	~19.00	~20.00	$ZnO_2 \cdot 2H_2O + ZnO_2 \cdot H_2O$
	28	46.54	10.94	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0.5H_2O$
	14	57.98	27.78	$ZnO_2 \cdot 0.5H_2O + ZnO_2$
	25	86.15	8.31	$ZnO_2 + ZnO_2 \cdot H_2O_2$
0	32	0.07	0.74	$Zn(OH)_2 + ZnO_2 \cdot 2H_2O$
	9	15.09	9.01	$ZnO_2 \cdot 2H_2O + ZnO_2 \cdot H_2O$
	36	28.34	5.23	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0.5H_2O$
	37	40.93	5.00	$ZnO_2 \cdot 0.5H_2O + ZnO_2$
	30	74.38	19.72	$ZnO_2 + ZnO_2 \cdot H_2O_2$
−10	21	20.43	4.37	$ZnO_2 \cdot H_2O + ZnO_2 \cdot 0.5H_2O$
	34	38.69	6.61	$ZnO_2 \cdot 0.5H_2O + ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$
	19	62.32	8.03	$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O + ZnO_2$
	33	72.65	2.30	$ZnO_2 + ZnO_2 \cdot H_2O_2$
−20	26	40.23	27.80	$ZnO_2 \cdot 0.5H_2O + ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$
	6	48.03	7.44	$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O + ZnO_2$
	24	70.78	7.82	$ZnO_2 + ZnO_2 \cdot H_2O_2$
	21	77.55	2.53	$ZnO_2 \cdot H_2O_2 + ZnO_2 \cdot 2H_2O_2$

SUMMARY

1. The system $Zn(OH)_2 - H_2O_2 - H_2O$ was studied at 30, 20, 0, −10, and −20° by the solubility method.

2. The true composition and succession of changes in the system $Zn(OH)_2 - H_2O_2 - H_2O$ were established from a general analysis of data for the diagrams $ZnO - H_2O - 1/2\ O_2$ and $ZnO - H_2O_2$ in the liquid phase.

3. In the system $Zn(OH)_2 - H_2O_2 - H_2O$ in the temperature range from 30° to −20° it may be considered provisionally that the following solid phases exist:

a) a series of hydrates of zinc peroxide:

$$ZnO_2 \cdot 2H_2O;\ ZnO_2 \cdot 1.5H_2O;\ ZnO_2 \cdot H_2O;\ ZnO_2 \cdot 0.5H_2O;$$

b) anhydrous zinc peroxide ZnO_2;

c) zinc peroxide monohydrate semiperhydrate:

$$ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O;$$

d) perhydrates of zinc peroxide:

$$ZnO_2 \cdot H_2O_2,\ ZnO_2 \cdot 2H_2O_2.$$

4. Comparison of our data on the system $Zn(OH)_2 - H_2O_2 - H_2O$ in the temperature range from 30° to − 20° with data in the literature (Figure 1) shows that the great majority of the peroxy compounds of zinc reported previously were probably mechanical mixtures.

5. The polythermal solubility diagram of the ternary system $Zn(OH)_2 - H_2O_2 - H_2O$ was constructed and enables the limits of existence of the solid phases of the system to be determined.

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KINETIC CHARACTERISTICS OF THE OXIDATION OF PROPANE WITH OXYGEN MIXED WITH CHLORINE IN QUARTZ VESSELS

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Among investigations on the homogeneous catalysis of the oxidation of hydrocarbons there are several on the initiating effect of additions of chlorine [1-5]. For example, Carman [1], working on the preparation of formaldehyde by the oxidation of methane, proposed to add chlorine to a gaseous mixture of oxygen and methane and carry out the reaction in presence of heterogeneous catalysts (beryllium, strontium, and calcium chlorides). Kreshkov [2] studied the oxidation of methane at high temperatures with a mixture of gaseous Cl_2 and steam, also in presence of various heterogeneous catalysts. It was suggested that oxidation of the methane was brought about by oxygen formed by the reaction:

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2.$$

It was clearly desirable to determine also the possibility of initiating the oxidation of hydrocarbons by small additions of chlorine in absence of solid surfaces known to have a catalyzing effect.

Maizus and Emanuel [3] showed that small additions of chlorine to a mixture of propane and oxygen are able to accelerate reaction appreciably and lower the temperature required for the process. The occurrence of an initiating effect was fairly natural, for chlorine atoms formed by the dissociation of molecular chlorine at the walls of the reaction vessel [4] are bound to react with hydrocarbon molecules with formation of free hydrocarbon radicals: $Cl + RH \rightarrow HCl + R$. These hydrocarbon radicals initiate the usual chain of elementary reactions: $R + O_2 \rightarrow RO_2$, $RO_2 + RH \rightarrow RO_2H + R$, etc. The general scheme for the oxidation process includes also the decomposition of the peroxy radical RO_2 with formation of aldehydes and ketones and the decomposition of peroxides, which act as molecular intermediate products.

In 1952, Zemlyansky, Prib, and Sharypkina [5] published the results of an investigation of the oxidation of methane by air in presence of chlorine. They established that chlorine additions lower the temperature required for the oxidation reaction of methane and increase the yields of formaldehyde and formic acid. As a simple method of initiating the oxidation of hydrocarbons, the use of additions of chlorine is of potential importance, and we decided to make a more careful examination of the chemical possibilities of initiation by chlorine. In connection with this problem we are publishing a series of papers on the effect of additions of chlorine on the oxidation of propane carried out in different ways (in vessels without a filling and made of various kinds of glass; in vessels with fillings).

EXPERIMENTAL

Procedure

The oxidation of propane with oxygen with additions of chlorine was studied in a flow apparatus at atmospheric pressure. A diagram of the apparatus is given in Figure 1.

Diagram of Experimental Flow Apparatus

A mixture of oxygen and chlorine was prepared in the flask 1 and was passed through the flowmeter 2 to the mixer 3. Propane passed to 3 through the flowmeter 4. An equimolecular mixture of propane and oxygen passed from 3 to the reaction vessel 5, which consisted of a clear quartz tube, 220 ml in volume.

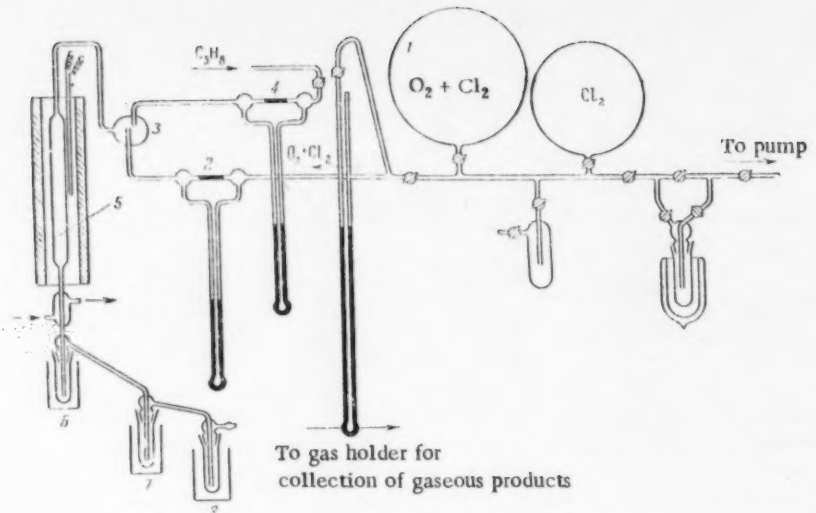

Fig. 1. Diagram of the experimental flow apparatus.

Before the experiment the reaction vessel was treated with chromic acid and steam. The liquid reaction products were condensed in the traps 6, 7, and 8, which were cooled with ice, and the gas was collected in a gas holder over saturated brine. The liquid products were analyzed for contents of acetaldehyde, formaldehyde, peroxides, organic acids, and HCl. The gaseous products were analyzed for unsaturated hydrocarbons, O_2, CO, and CO_2 in a VTI apparatus.

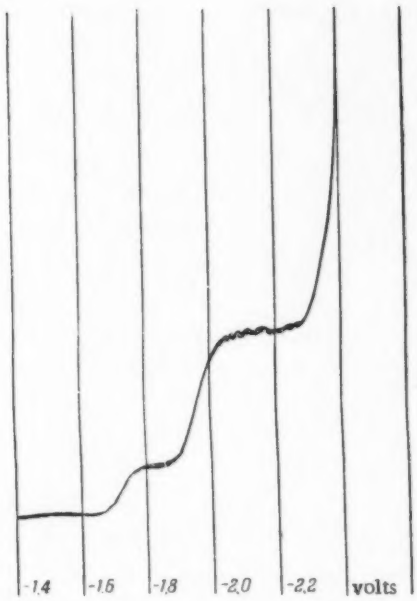

Fig. 2. Polarogram of condensate obtained by oxidizing propane with oxygen containing 1.5% of chlorine (supporting electrolyte 0.1 N LiOH).

The total amount of carbonyl compounds was determined by the usual hydroxylamine method (reaction of hydroxylamine hydrochloride with carbonyl compounds). We showed that the error in the determination of carbonyl compounds due to the presence of peroxides, which also react with hydroxylamine hydrochloride, did not exceed 3-5% under our conditions. Aldehydes were determined polarographically. It was shown in special experiments that chlorine does not interfere in the polarographic determination of aldehydes. Figure 2 shows a typical polarogram of the condensate, taken in 0.1 N LiOH. There are two distinct waves: at -1.6v, which corresponds to the reduction of formaldehyde; and at -1.8 v, which corresponds to the reduction of acetaldehyde. Under these conditions peroxides are not reduced; they were determined iodometrically and polarographically. We used the polarographic method for the identification of the peroxides. The polarogram of the condensate determined in 0.1 N LiCl with prior passage of hydrogen is given in Figure 3. The quantitative determination of peroxides was carried out iodometrically. In view of the fact that chlorine also effects the liberation of iodine, it was

necessary to assess the error in the determination of peroxides due to the presence of chlorine in the gas mixture. If it is assumed that the whole of the chlorine added passes into the condensate as free chlorine, then even in this case we obtain an error in the determination of peroxides of less than 1%. We showed that, owing to the high solubility of chlorine in water and its consumption in the course of the reaction, the actual error was not more than a few tenths of one percent. Organic acids were determined from the difference in the amount of 0.1 N NaOH required in the titration of all the acids (to phenolphthalein) and the amount required in the titration of HCl (to Bromophenol blue).

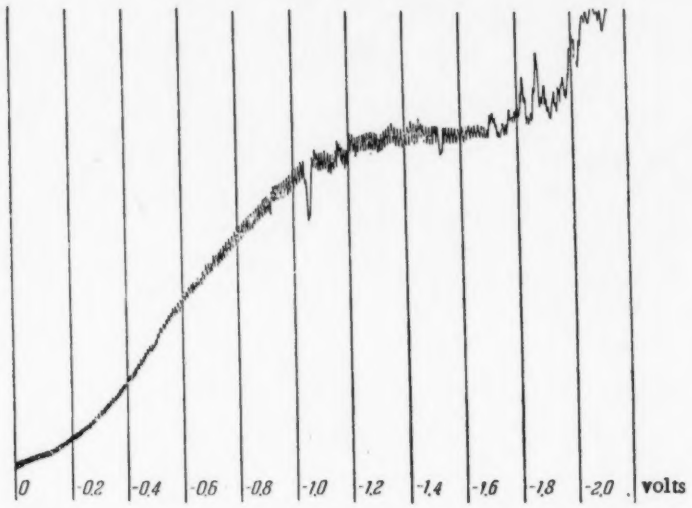

Fig. 3. Polarogram of the condensate obtained by oxidizing propane with oxygen containing 1.5% of chlorine (supporting electrolyte 0.1 N LiCl)

The results of all analyses were expressed as amount of propane (%) necessary for the formation of the respective oxidation products.

Experimental Results

Figure 4 gives the kinetic curves for the formation of products of the oxidation of propane with an equimolecular proportion of oxygen containing 1.5% of chlorine by volume in a quartz vessel without filling at 310°. It is noteworthy that an appreciable amount of peroxides (up to 7%) is formed, whereas in the uncatalyzed oxidation of propane the concentration of peroxides does not exceed 1% by volume. The contents of acetaldehyde, formaldehyde, organic acids, and peroxides attain their maximum values in about one minute. The peroxides, being molecular intermediate products, are consumed, but acetaldehyde, formaldehyde, and organic acids preserve their maximum yields unchanged in the further course of the oxidation process. Among the gaseous products of the reaction, CO_2 (up to 0.5%), CO (up to 4.5%), and unsaturated hydrocarbons (up to 9%) were determined. It must be emphasized that, when the oxidation reaction is carried out in a quartz reaction vessel without filling, a long period of contact – attaining several minutes – is necessary. Flow experiments under such conditions are, of course, similar to static experiments, since the rate of back diffusion of the reacting mixture exceeds the linear velocity of the reactants in the reaction vessel.

We investigated the effects of temperature and amount of added chlorine on the oxidation of propane with oxygen. Rise in temperature had different effects on the various reaction products. Figure 5 shows the effects of temperature and amount of added chlorine on the kinetics of peroxide formation. It is clearly seen that with rise in temperature from 250° to 355° the amount of peroxides in the oxidation products increases appreciably, but the time required for the attainment of maximum concentration of peroxides is reduced, i.e., the kinetic curves are displaced toward shorter times of contact.

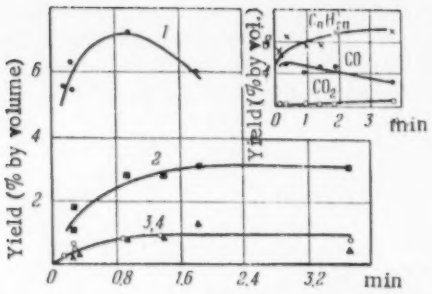

Fig. 4. Kinetic curves for the formation of reaction products in the oxidation of an equimolecular mixture of propane and oxygen with an addition of 1.5% of chlorine (310°): 1) peroxides; 2) acetaldehyde; 3) formaldehyde; 4) organic acids (Figure 4 shows also the change in the concentrations of CO, CO_2, and C_nH_{2n} unsaturated hydrocarbons in the course of the process).

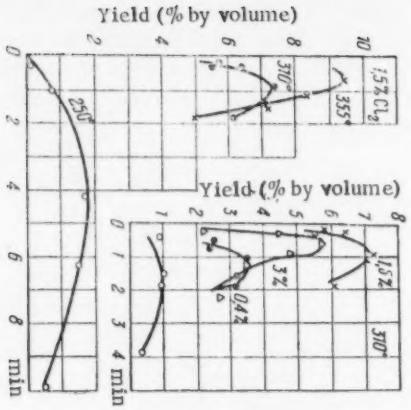

Fig. 5. Effects of temperature and amount of added chlorine on the yield of peroxides.

Increase in the amount of chlorine added has a very similar effect. With increase in the chlorine content of the mixture from 0 to 1.5% a great increase in the yield of peroxides is observed and the kinetic curves are displaced toward the time origin. However, with further increase in chlorine content (up to 3%), some reduction in the maximum yield of peroxides occurs, although the maximum is still displaced toward the time origin. It would appear that chlorine initiates not only the formation of peroxides, but also their further transformation. The fact that rise in temperature and increase in the amount of chlorine added act in the same direction enables us to understand, qualitatively, why the reaction in presence of chlorine can be carried out at a lower temperature than the uncatalyzed oxidation process. It should be noted also that the kinetic curve for the formation of peroxides in a mixture not containing chlorine was determined in experiments in the same reaction vessel as that used here for reaction catalyzed by chlorine. Our later experiments showed that chlorine has a definite after-effect due to modification of the surface of the vessel by the reaction. The yields of peroxides in an ostensibly uncatalyzed process were therefore somewhat greater than in "fresh" vessels. However, in spite of this modification of the surface of the vessel, uncatalyzed reaction gives comparatively low yields of peroxides.

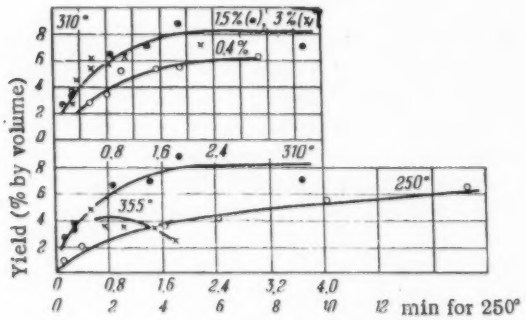

Fig. 6. Effects of temperature (1.5% of chlorine in mixture) and amount of chlorine added (at 310°) on the total yield of aldehydes.

It was important to identify the peroxides formed in the chlorine-catalyzed oxidation of propane. We showed that the peroxide that we determined consisted of a mixture of isopropyl hydroperoxide and hydrogen peroxide. With rise in temperature, and also with change in the material from which the vessel was constructed, the hydrogen peroxide content increased. Particularly high contents of hydrogen peroxide were obtained in vessels having no filling and made of molybdenum glass. In the present case we are concerned mainly with isopropyl hydroperoxide, hydrogen peroxide being present in relatively small amounts. This will be particularly clear from an examination of the polarogram of the condensate taken in 0.1 N LiCl with prior passage of hydrogen (Figure 3). This polarogram is practically coincident with that obtained for pure isopropyl peroxide by Fok and Nalbandyan [6]. Also, the peroxide was identified by decomposition with HBr; in this reaction isopropyl peroxide gives

acetone [6]. The experiment was carried out as follows. The mixture of reaction products was passed from the reaction vessel to a second quartz tube at 100°. Hydrogen bromide was added, and as a result of reaction there was an increase in the amount of carbonyl compounds, which must be attributed to the appearance of acetone. When in the first vessel, the reaction product contained 3.5% of carbonyl compounds, 1.7% of acetaldehyde, and 2.6% of peroxides. After passage through the second vessel, the total content of carbonyl compounds increased to 5.6%, that of acetaldehyde increased to 1.9% and the content of peroxides fell to 0.7% i.e. the destruction of 1.9% of peroxides resulted in an approximately corresponding increase in the content of carbonyl compounds (by 2.1%).

Figure 6 shows the effects of temperature and of added chlorine on the kinetics of the formation of carbonyl compounds. Rise in temperature from 250° to 310° causes an increase in the rate of formation of carbonyl compounds. However, further rise in temperature to 355° results in a fall in the maximum yield of carbonyl compounds. This fact is probably associated with increase in the rate of their further oxidation, and there is, in fact, an increase in the amounts of CO and CO_2 in the gaseous reaction products (Figure 8). Increase in the addition of chlorine from 0.4% to 1.5% has a favorable effect on the yield of aldehydes, but there is no further effect when the amount of chlorine is raised further to 3%. From this it may be inferred that it is undesirable to make large additions of chlorine in the propane-oxidation reaction – all the more in that the amounts of the final reaction products, CO and CO_2, are substantially increased under these conditions (Figure 8).

Examination of the effects of temperature and additions of chlorine on the kinetic curves for the formation of organic acids (Figure 7) shows that additions of chlorine act similarly to rise in reaction temperature. Rise in temperature from 250° to 310° increases the yield and rate of formation of organic acids. The same is observed as we pass from 0.4% to 1.5% of added chlorine. However, further rise in temperature from 310° to 355° (or increase of chlorine content from 1.5% to 3%) has no effect on the kinetics of formation of organic acids.

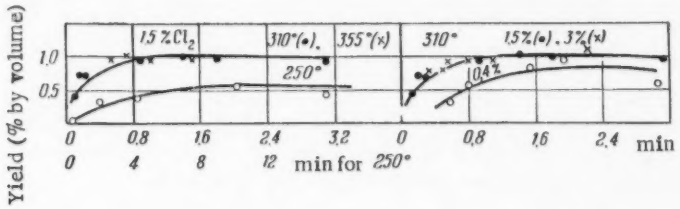

Fig. 7. Effects of temperature and amount of added chlorine on the yield of organic acids.

We again come to the same conclusion regarding the parallelism between additions of chlorine and rise in reaction temperature as in the case of the formation of carbonyl compounds. In both cases we have identical maximum yields of products, which can be attained by either of the stimulants – additions of chlorine or rise in temperature. Thus, for the formation of organic acids the maximum yield is 1% (conversion of propane into acids) for both methods of stimulation; for carbonyl compounds it is 8%. The only difference in the effects of chlorine and of temperature on the formation of carbonyl compounds is that increase in chlorine content above a certain value (1-1.5%) does not lower the maximum yield, whereas rise in temperature (above 310°) causes a lowering of yield. These differences, however, are probably associated with additional complications in the process which arise when the chlorine content of the reacting mixture is considerably increased.

In Figure 8, apart from the above-mentioned kinetic curves for the formation of CO and CO_2, curves are shown also for the formation of unsaturated compounds at various temperatures. It will be seen from Figure 8 that rise in temperature from 250° to 310° causes an appreciable increase in the extent to which unsaturated hydrocarbons are formed. However, further rise in temperature (from 310° to 355°) has a much smaller effect on the yield of unsaturated compounds.

It must be pointed out also that, in spite of the formation of readily oxidized substances such as aldehydes, the kinetic curves for these products, as also for the gaseous products, tend to limiting values. This again indicates the presence of a complex system of retarding processes in the oxidation of hydrocarbons. The

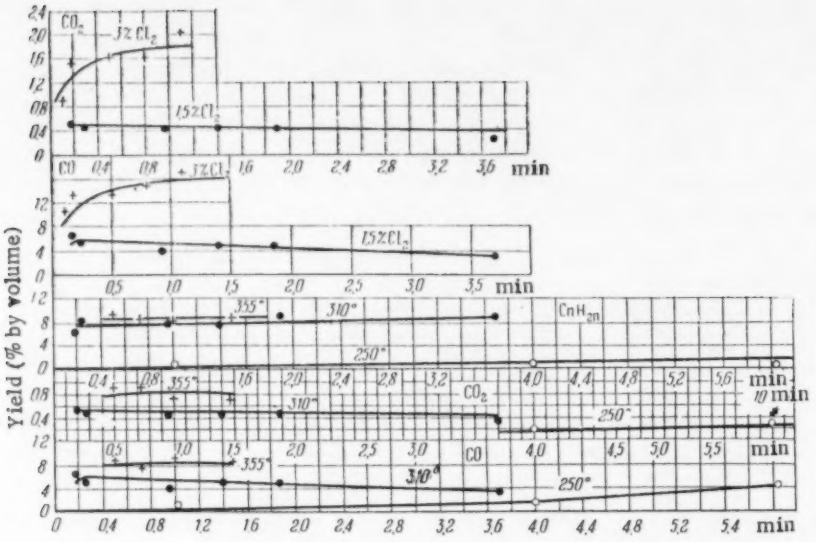

Fig. 8. Kinetic curves for the formation of gaseous products at various temperatures and for different additions of chlorine.

elucidation of such retarding effects and of the ways in which they can be eliminated is an important problem of chemical kinetics.

Discussion of Experimental Results

Our experimental results show that additions of chlorine increase the yield of oxygen-containing products, in particular peroxides. It was important to determine at what stage of the reaction the effect of the addition of chlorine comes into play. It is known from the literature that the oxidation of propane is a chain reaction with degenerate branching, so that the acceleration of the process may be associated both with chain-initiation and chain-branching reactions.

In this connection let us examine two of the schemes that have been assumed in the literature for oxidation processes (in their application to the oxidation of propane) with the view of establishing the relation of the maximum yield of peroxy compounds both to the rate of chain initiation w_0, and also to the rate of chain branching. The basis of one of one of these schemes lies in the stage examined by Shtern [7], in which aldehydes are formed as a result of elementary isomerization reactions and decomposition of the peroxide radical RO_2. The basis of the other lies in the formation of aldehydes from molecular intermediate compounds of a peroxide nature. In both schemes degenerate branching is associated with oxidation of aldehydes.

Let us examine the first scheme (aldehydes are formed by the decomposition of a peroxide radical RO_2):

$$RH + O_2 \rightarrow HO_2 + R \text{ (initiation)} \quad (0)$$

$$R + O_2 \rightarrow RO_2 \text{ (propagation)} \quad (1)$$

$$RO_2 \rightarrow \text{aldehyde} + R \quad (2)$$

$$RO_2 + RH \rightarrow ROOH + R \quad (3)$$

$$ROOH \rightarrow \text{oxidation product} \quad (4)$$

$$\text{Aldehyde} \rightarrow \text{oxidation product} \quad (5)$$

$$\text{Aldehyde} + O_2 \rightarrow R + HO_2 \text{ (degenerate branching)} \quad (6)$$

$$RO_2 \rightarrow \text{wall (termination)} \quad (7)$$

The exothermic reaction (1) goes almost without activation energy ($\epsilon_1 \approx 0$), so that for the rate constant of this elementary reaction we may assume the value

$$k_1 = 10^{-1} \text{ cc/sec}$$

In the reaction of unimolecular decomposition of the radical RO_2 (2), Semenov considers that the limiting stage is the isomerization of the radical RO_2, which requires an activation energy ϵ_2 of the order of 20 kcal/mole [8]. Assuming that $\epsilon_2 = 20$ kcal/mole, we may calculate the rate constant k_2 for the temperature that interests us, 523°K:

$$k_2 = 10^{13} e^{-\frac{20000}{2 \cdot 523}} = 10^5 \text{ sec}^{-1}.$$

The rate constant for reaction of the radical RO_2 with a hydrocarbon molecule (Reaction 3) may be evaluated if we take into account that activation energies for these reactions are 5-10 kcal/mole [8]. Assuming that $\epsilon_3 = 10$ kcal/mole, we find that

$$k_3 = 10^{-10} e^{-\frac{10000}{2 \cdot 523}} = 0{,}8 \cdot 10^{-14} \text{ cc/sec}.$$

In our evaluation of the rate constant of stage (4), having no data on the rate of this stage, we shall assume that it is of the same order as the rate of primary decomposition of the hydroperoxide into radicals. This can be evaluated from the usual formula for the rate constant of a unimolecular reaction:

$$k_4 = 10^{13} e^{-\frac{\epsilon_4}{RT}},$$

in which ϵ_4 is the energy of rupture for the O — O bond. It is known that for complex peroxides the rupture energy is 30-35 kcal/mole [8].

Hence

$$k_4 = 10^{13} e^{-\frac{35000}{2 \cdot 523}} = 0.4 \text{ sec}^{-1}.$$

It may be expected that the bimolecular reaction (6) of aldehyde with oxygen, as a reaction with a diradical molecule, proceeds without activation energy and that the apparent activation energy of this process is simply the absolute value of the heat of reaction q_6, which may be calculated from the bond energy consumed in the elementary act of reaction:

$$q_6 = Q_{H-O_2} - Q_{\underset{\text{ald}}{C-H}} = 45 - 85 = -40 \text{ kcal}.$$

since the C — H bond energy is given as 85 kcal in Szwarc's tables [9], and the energy of combination of H and O_2 is 45 kcal [8]

$$\epsilon_6 = |q_6| = 40 \text{ kcal/mole}$$

$$k_6 = 10^{-10} e^{-\frac{40000}{2 \cdot 523}} = 10^{-25} \text{ cc/sec}$$

The constant of linear termination k_7 is generally taken as

$$k_7 = 1 \text{ sec}^{-1}$$

By writing the equation for rates of formation of active centers and assuming their concentration to be stationary, we may readily find an expression for the dependence of the maximum yield of peroxide on the rate of formation of active centers w_0 and on the rate of the branching reaction. We may, in fact, write the following system of equations:

$$\frac{d(R)}{dt} = w_0 - k_1(R)(O_2) + k_2(RO_2) + k_3(RO_2)(RH) + k_6(\text{ald.})(O_2);$$

$$\frac{d(RO_2)}{dt} = k_1(R)(O_2) - k_2(RO_2) - k_3(RO_2)(RH) - k_7(RO_2);$$

$$\frac{d(ROOH)}{dt} = k_3(RO_2)(RH) - k_4(ROOH).$$

Simultaneous solution of the equations

$$\frac{d(R)}{dt} = 0 \text{ and } \frac{d(RO_2)}{dt} = 0,$$

gives

$$(RO_2) = \frac{w_0 + k_6(ald)(O_2)}{k_7}$$

Substituting the value of (RO_2) in the expression for $\frac{d(ROOH)}{dt}$, we find

$$\frac{d(ROOH)}{dt} = \frac{k_3[w_0 + k_6(ald)(O_2)]}{k_7}(RH) - k_4(ROOH).$$

As we are interested in the dependence of the maximum yield of peroxide on w_0 and on the rate of the chain-branching reaction, we shall assume

$$\frac{d(ROOH)}{dt} = 0,$$

from which we obtain

$$(ROOH)_{max} = \frac{k_3}{k_4 k_7}(RH)[w_0 + k_6(\text{aldehyde})(O_2)] = \alpha[w_0 + k_6(\text{aldehyde})(O_2)]$$

Assuming the value $k_6 = 10^{-25}$ cc/second found above, and calculating from elementary data the concentrations

$$(O_2) = 0.7 \cdot 10^{19} \text{ molecules/cc}$$

and

$$(ald) = 5.1 \cdot 10^{17} \text{ molecules/cc}$$

we obtain for the rate of branching:

$$k_6(\text{aldehyde})(O_2) = 10^{-25} \cdot 0.7 \cdot 10^{19} \cdot 5.1 \cdot 10^{17} = 0.4 \cdot 10^{12} \text{ molecules/cc} \cdot \text{second}$$

so that

$$(ROOH)_{max} = \alpha(w_0 + 0.4 \cdot 10^{12})$$

The order of w_0 can be estimated on the assumption that the reaction of active-center formation is the process $RH + O_2 \rightarrow R + HO_2$. Assuming that the activation energy of this process is equal to its endothermicity, we obtain:

$$\epsilon_0 = |q_0| = |Q_{H-O_2} - Q_{R-H}|.$$

The C – H bond energy in the methyl of propane is 95 kcal/mole, and that of the methylene group is 79 kcal/mole [9]. The energy of the addition of H to O_2 is 45 kcal/mole [8].

$$q_0 = Q_{H-O_2} - Q_{R-H} = 45 - 85 = -44^{*} \text{ kcal},$$

* As in original. The numerical discrepancy which occurs here is apparently carried over into the following equations – Publisher's note.

so that

$$\epsilon_0 = |q_0| = 44 \text{ kcal/mole},$$

and therefore

$$k_0 = 10^{-10} e^{-\frac{44\,000}{2 \cdot 523}} = 10^{-27} \text{ cc/sec}$$

and

$$w_0 = k_0 (RH)(O_2) = 10^{-27} \cdot 0.7 \cdot 10^{19} \cdot 0.7 \cdot 10^{19} = 0{,}1 \cdot 10^{12} \text{ molecules/cc} \cdot \text{sec}$$

in which

$$(RH) = 0.7 \cdot 10^{19} \text{ molecules/cc and } (O_2) = 0.7 \cdot 10^{19} \text{ molecules/cc}.$$

Hence, the rate of formation of active centers is of the same order of magnitude as the rate of branching, but the latter is somewhat greater than the former – as it should be.

We shall now evaluate the value of α. From the experimental data, for the maximum concentration of peroxides we have the value $2.4 \cdot 10^{17}$ molecules/cc[3].

$$2.4 \cdot 10^{17} = \alpha (0.1 \cdot 10^{12} + 0.4 \cdot 10^{12});$$

$$\alpha = \frac{2.4 \cdot 10^{17}}{0.5 \cdot 10^{12}} = 4.8 \cdot 10^5,$$

which is in good agreement with the value of α calculated with the aid of the values we have accepted for the constants of the elementary reactions:

$$\alpha = \frac{k_3}{k_4 k_7}(RH) = \frac{0.8 \cdot 10^{-14}}{0.4 \cdot 1} \quad (0.7 \cdot 10^{19}) = 1.4 \cdot 10^5.$$

As a result we obtain a final expression for the maximum concentration of peroxy compounds:

$$(ROOH)_{max} = 1.4 \cdot 10^5 (w_0 + 0.4 \cdot 10^{12}). \qquad (1)$$

It can be seen directly from this formula that the value of $(ROOH)_{max}$ must increase both under conditions that favor increase in the rate of chain initiation and also under conditions that favor increase in the rate of the branching reaction. We have succeeded in showing (these experiments will be discussed in our future publications) that additions of chlorine, while increasing $(ROOH)_{max}$, have no effect on the autocatalytic character of the kinetic curves of the intermediate reaction products. This can be explained only on the assumption that addition of chlorine does not affect the rate of the branching reaction, but increases w_0. Equation 1 requires linear dependence of $(ROOH)_{max}$ on w_0. In fact, however, the experiment relationship between maximum yield of peroxy compounds and amount of chlorine added has a maximum. For small additions of chlorine the yield rises in accordance with a law which is very roughly linear, but with further increase in the chlorine content of the mixture the maximum peroxide concentration falls. This result must evidently be explained by the occurrence of a variety of secondary processes of interaction between chlorine and peroxides. In any case, small additions of chlorine increase $(ROOH)_{max}$ and this clearly occurs as a result of increase in the rate of initiation of chains. As regards the increase of $(ROOH)_{max}$ with rise in temperature, which can be seen in Fig. 5, this effect is undoubtedly due to two factors – increase in ω_0 and increase in the rate of chain branching, since the rates of both these elementary stages increase with rise in temperature.

Let us now examine the second possible oxidation scheme, in which aldehydes are formed by the decomposition of molecular intermediate products of peroxide character. We have no right to exclude such a possibility, for reaction in this direction predominates in processes of low-temperature liquid-phase oxidation. Moreover, there is as yet no unequivocal evidence in favor of the first scheme. In accordance with our discussion, the second scheme has the following form:

$$RH + O_2 \rightarrow R + HO_2 \text{ (initiation)} \quad (0)$$
$$R + O_2 \rightarrow RO_2 \quad (1)$$
$$RO_2 + RH \rightarrow ROOH + R \text{ (propagation)} \quad (2)$$
$$ROOH \rightarrow \text{aldehyde} \quad (3)$$
$$\text{Aldehyde} \rightarrow \text{product} \quad (4)$$
$$\text{Aldehyde} + O_2 \rightarrow R + HO_2 \text{ (degenerate branching)} \quad (5)$$
$$RO_2 \rightarrow \text{wall (termination)} \quad (6)$$

It is not difficult to see, however, that this scheme will lead to the same formula for $(ROOH)_{max}$ as the first scheme did. In fact, the method of stationary concentrations gives

$$\frac{d\,(ROOH)}{dt} = k_2\,(RO_2)\,(RH) - k_3\,(ROOH)$$

and

$$(RO_2) = \frac{w_0 + k_5\,(ald)\,(O_2)}{k_6},$$

so that for $(ROOH)_{max}$ we have

$$(ROOH)_{max} = \frac{k_2}{k_3 k_6}\,(RH)\,[w_0 + k_5\,(ald)\,(O_2)]$$

or, assuming that

$$\alpha = \frac{k_2}{k_3 k_6}\,(RH),$$

we finally obtain

$$(ROOH)_{max} = \alpha\,[w_0 + k_5\,(ald)\,(O_2)],$$

in which

$$k_5\,(ald)\,(O_2) = 0.4 \cdot 10^{12} \text{ molecules/cc} \cdot \text{second};$$

$$(ROOH)_{max} = \alpha\,(w_0 + 0.4 \cdot 10^{12}),$$

i.e., the same result as Equation 1. Hence, all our considerations relating to the character of the effects of additions of chlorine and change of temperature retain their validity irrespective of which chemical mechanism we assume for the oxidation process.

SUMMARY

1. A study was made of the oxidation of propane with oxygen mixed with chlorine under flow conditions in a quartz vessel without filling attemperatures of 250°, 310°, and 355°.

2. It was shown that small additions of chlorine accelerate the oxidation of propane and increase the yield of oxygen-containing products. It was found that large additions of chlorine are undesirable, for the yields of valuable oxygen-containing products are not increased and far-reaching oxidation (combustion) processes are stimulated.

3. It was found that one of the molecular intermediate products was an organic peroxide (isopropyl hydroperoxide), which was formed in considerable amount.

4. Schemes proposed in the literature for the oxidation of hydrocarbons were examined in their application to the oxidation of propane, and it was shown that the effect of additions of chlorine is to be attributed mainly to increase in the rate of formation of initiating centers.

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THERMOGALVANIC CORROSION

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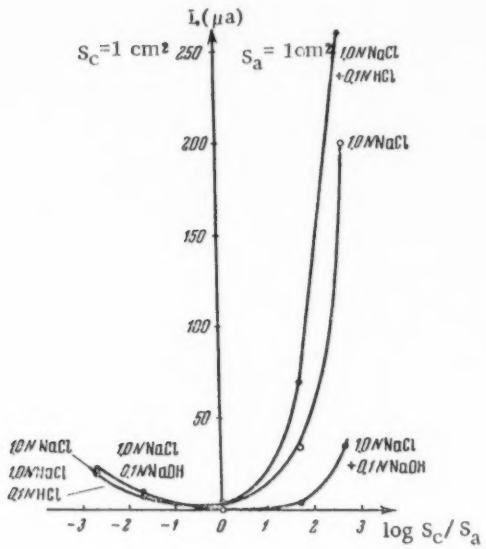
Thermogalvanic corrosion results from the action of a macrocouple formed when different pieces of the same metal immersed in an electrolyte have different temperatures. The piece of metal that forms the anode in such a macrocouple becomes corroded.

It has been shown [1-4] that the extent of thermogalvanic corrosion depends on the potential difference between the cold and hot electrodes, the electrical conductivity of the solution, the distance between the electrodes, and the overvoltages of the anode and cathode processes. In the present work we investigated the thermogalvanic corrosion of iron, copper, nickel, and lead in neutral, alkaline, and acid solutions for different temperature differences and relative electrode areas, and with and without stirring of the electrolyte.

EXPERIMENTAL

The two electrodes were in vessels contained in thermostats, one at 80-50° (hot electrode) and one at 20° (cold electrode). The corrosion was estimated from the current flowing between the electrodes. It was found that the hotter electrode was always the anode.

The figure shows the dependence of the current from a copper thermogalvanic couple on the relative areas of the cold and hot electrodes. It will be seen that, in an alkaline medium (1.0N NaCl + 0.1 N NaOH), the current from a copper thermogalvanic couple is increased both by increase in the area of the cathode S_c and by increase in the area of the anode S_a. It is evident that in this case corrosion proceeds with mixed (anode and cathode) control. In neutral (1.0 N NaCl) and acid (1.0 N NaCl + + 0.1 N HCl) media, with increase in the area of the cold electrode (cathode), the current from the couple increases to a much greater extent than it does when the area of the anode is increased. This indicates that in these media corrosion proceeds with cathode control. Similar phenomena were observed for the thermogalvanic corrosion of iron, nickel, and lead in all the media investigated.



Effect of change in the areas of the electrodes on the current of the thermogalvanic couple (copper).

In an acid medium, owing to the occurrence of corrosion as a result of hydrogen depolarization, the rate of the cathode process on the metals investigated was generally higher than in an alkaline or neutral medium. The rate of thermogalvanic corrosion was therefore higher in 1.0 N NaCl + 0.1 N HCl than in other

TABLE 1

Rate of Thermogalvanic Corrosion for Different Relative Areas of Cathode and Anode ($\times 10^{-4}$ g/sq. cm per day)

$\frac{S_c}{S_a}$	$\log \frac{S_c}{S_a}$	1.0 N NaCl				1.0 N NaCl + 0.1 N HCl				1.0 N NaCl + 0.1 N NaOH			
		Cu	Ni	Fe	Pb	Cu	Ni	Fe	Pb	Cu	Ni	Fe	Pb
$\Delta T = 60°$													
500 : 1	2.7	56.7	13.0	75.0	39.1	73.1	326.0	327	320	9.9	1.30	390	184
50 : 1	1.7	9.9	1.05	20.0	10.1	19.7	62.5	45	59	1.13	0.16	39.0	51
1 : 1	0	0.68	0.056	1.28	1.79	0.817	1.83	2.3	1.97	0.35	0.004	1.28	2.2
1 : 50	−1.7	0.085	0.0053	0.25	0.18	0.045	0.117	0.10	0.44	0.062	0	0.04	0.68
1 : 500	−2.7	0.011	0.0001	0.08	0.09	0.011	0.002	1.07	0.13	0.010	0	0.02	0.09
$\Delta T = 30°$													
1 : 1	0	0.25	0.018	0.7	1.1	0.42	1.44	0.83	0.75	0.254	0.0024	0.6	0.96

media (Table 1). An exception was formed by lead in an alkaline medium, in which the dissolution of protective films formed on the surface resulted in an increase in the rate of the cathode process, the effective surface of the cathode being increased. Table 1 gives data on the corrosion losses of the metals investigated in their dependence on the areas of the electrodes of the thermogalvanic macrocouple (S_c / S_a). It follows from Table 1 that, for a given temperature difference, the rate of thermogalvanic corrosion rises with increase in the area of the cold electrode (the cathode) in all media.

Stirring of the electrolyte in the cathode space greatly increases the rate of corrosion in thermogalvanic couples for which the controlling factor is the rate of diffusion of oxygen (lead in neutral and alkaline media, and iron in neutral media; see Table 2). In those cases in which the limiting factor is the ionization of oxygen or in which, apart from oxygen depolarization, discharge of hydrogen ions is possible, stirring the electrolyte in the cathode space has less effect on the extent of corrosion (copper and nickel in an acid medium, iron and nickel in an alkaline medium). Stirring the electrolyte in the anode space has little effect on corrosion losses. Stirring with passage of oxygen causes passivation of nickel in 1.0 N NaCl and of iron in neutral and alkaline media; the corrosion current is somewhat reduced in consequence. In the remaining cases stirring of the electrolyte in the anode space has almost no effect on the current from the thermogalvanic couple. An exception is formed by copper in an alkaline medium, in which stirring of the electrolyte in the anode space facilitates the dissolution by alkali of cupric hydroxide, cuprous oxide, and other compounds formed at the anode during corrosion; these compounds dissolve in the form of complex salts, and there is a resulting increase in the corrosion current. The blue-violet color of the electrolyte in the anode space indicates the presence of the complex salts $NaHCuO_2$ and Na_2CuO_2. Stirring of the electrolyte in the cathode space increases the rate at which hydroxyl ions are presented to the copper surface, which facilitates

TABLE 2

Effect of Stirring on the Current from a Thermogalvanic Corrosion Couple (temperatures 80° and 20°; the current in absence of stirring is taken as 100%

Metal	1.0 N NaCl		1.0 N NaCl + + 0.1 N HCl		1.0 N NaCl + + 0.1 N NaOH	
	cathode	anode	cathode	anode	cathode	anode
Pb	500	100	120	102	900	100
Cu	170	100	113	108	10	310
Ni	150	80	170	100	100	100
Fe	300	88	160	98.0	105	71

the formation of a compact black protective film and the covering of the active sites. This results in a reduction of the current from the couple. The black color of the film indicates that it consists predominantly of cupric oxide.

SUMMARY

1. Measurements were made of the currents from copper, nickel, iron, and lead thermogalvanic couples in neutral, alkaline, and acid solutions for different temperature differences and different relative areas of cathode and anode.

2. It was shown that the hot electrode is always the anode. The corrosion process proceeds with cathode control, except in the case of copper in an alkaline medium, for which the control is mixed. In an acid medium, in which the cathode process is fast, with rare exceptions thermogalvanic corrosion is greater than in neutral and alkaline media.

3. Stirring of the electrolyte and increase in the area of the cold electrode (the cathode) result in a sharp rise (by a factor of tens or hundreds) in the rate of thermogalvanic corrosion.

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DETERMINATION OF THE SPECIFIC SURFACE OF A CATALYST UNDER FLOW CONDITIONS FROM A SINGLE MEASUREMENT OF ADSORPTION EQUILIBRIUM

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The extensive use of adsorption methods of determining specific surfaces in the usual investigations on catalysis is prevented by the complexity of the technique (necessity for special high-vacuum apparatus and optical reading devices) of determining adsorption isotherms and by the long time required for these measurements. A very substantial simplification of the apparatus can be effected by measuring adsorption isotherms at atmospheric pressure under flow conditions with an inert gas as carrier; in this way results are obtained which agree quite satisfactorily with those obtained in a high-vacuum apparatus [1]. This can be seen from Fig. 1, in which the ordinate is S_d, denoting specific surfaces determined in the investigation cited from measurements of the adsorption of benzene vapor by many catalysts under flow (dynamic) conditions, and the abscissa is S, denoting specific surfaces determined from isotherms measured in a vacuum apparatus containing a quartz spring balance (and in some cases S_I, determined from the adsorption of iodine from its solution in carbon tetrachloride). These results show that the departure of the experimental points from the straight line corresponding to complete agreement between the results of the two methods exceeds 10% (the limits for this departure are indicated by the broken lines) only when S is very small and in one other case – for S = about 140 sq. m/g. There are adequate grounds for considering that the accuracy of the determination of specific surfaces from isotherms measured under flow conditions is close to that of measurements on the same adsorbate by the vacuum method.

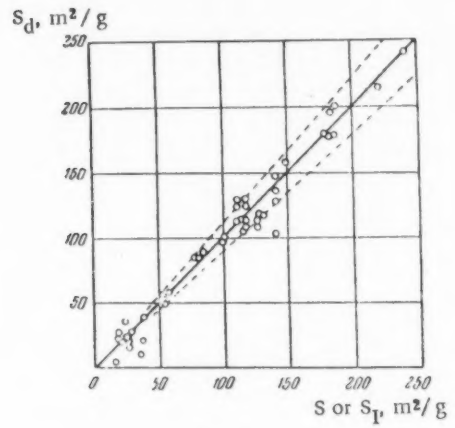

Fig. 1.

The possibility of greatly shortening the time required for the determinations became evident with the recent publication of papers showing that quite satisfactory and reproducible values of specific surface can be obtained from a single point on the isotherm in the section corresponding to an incomplete monolayer. On the basis of these investigations [2-4], in which the BET equation [5] is applied in a modified form, it is possible to solve the important problem of rapid multiple or routine determinations.

In one of these papers [2] a method was proposed for the experimental determination and calculation of specific surfaces on the assumption that the specific surface is proportional to the time required for the establishment of adsorption equilibrium at a given p/p_s The author constructed an apparatus in which this period of time was registered automatically. The determinations were carried out at the temperature of liquid nitrogen, measurements being made of the adsorption of nitrogen vapor, slowly introduced into the adsorber until equilibrium was attained at $p/p_s = 0.2$.

In a recently published paper [3], the specific surface was calculated from a single measurement of adsorption equilibrium made in the range of relative pressure 0.15-0.35, the equation used being:

$$\sum = \frac{[a(p_1 - p_2) - bp_2][760 - p_2] \cdot 9.85 \cdot 10^4}{760g}, \quad (1)$$

in which p_1 is the initial pressure of adsorbate in the system; p_2 is the pressure at adsorption equilibrium; g is the weight of adsorbate taken (g); a is a constant depending on the volume of the apparatus V (a = V/RT); b is a quantity depending on the porosity of the sample and serving as a coefficient in the correction for dead space; and $9.85 \cdot 10^4$ is the area (sq.m) occupied by one mole of nitrogen on the surface (for a molecular area of 16.2 A). The author remarks that this rapid method is to be recommended for use only after preliminary experiments with the particular adsorbent-adsorbate system concerned. Under favorable conditions (when c of the BET equation is greater than 100) the results obtained show departures of about 4% from those obtained by the BET method.

In the most recent paper on this subject [4] Temkin established experimentally for a large number of adsorbents that the ratio of the amount of nitrogen vapor adsorbed under given conditions to the amount corresponding to a monolayer (in the range of applicability of the BET adsorption isotherm) is constant, and he proposed a method for the calculation of specific surface from a single measurement of adsorption equilibrium, the equation used being:

$$V_m = V(1 - p/p_s)\left(1 + \frac{(p_s/p) - 1}{c}\right), \quad (2)$$

in which the symbols have the same meaning as in the BET equation. Temkin checked this equation by determining the specific surfaces of several catalysts by the low-temperature adsorption of nitrogen. In view of the great simplicity of this method and the high speed of measurement, it was considered to be desirable to determine to what extent it is applicable to adsorption of benzene vapor under flow conditions at ordinary temperature and pressure, and this we have done.

EXPERIMENTAL

The procedure, including preparation of the samples for the determination, and the apparatus for the measurement of the adsorption isotherms of benzene or carbon tetrachloride vapor at atmospheric pressure in a flow system were described in a previous paper [1]. In the present work we used a much more compact adsorption component, which is shown diagrammatically in Figure 2. The great advantage of such an arrangement over that used previously lies in the reduction of the dead space to a minimum, this being effected by causing the whole of the stream of carrier gas + adsorbate vapor to pass through the adsorbent. In this section of the apparatus a is the saturator, b is the mixer, in which nitrogen saturated with benzene vapor is diluted with pure nitrogen in order to establish the required value to p/p_s, c is the adsorption section proper, and in this there is a joint d carrying a tube e, which contains the sample and is closed with ground stoppers during weighing.

In order to apply Equation 2 to the experimental data it is necessary to find the values of the constant c and $\Delta E = E_1 - E_L$ at the temperature of the determinations. In our experiments the adsorbate was benzene and its adsorption was measured at 20°. The values of ΔE and c were calculated from data given in Afanasyev's dissertation [6] and in the paper [1]. They were found to be 471 ± 50 cal/mole and 21, respectively. With the aid of Equation 2 with the value found for c, values of V/V_m were calculated for a series of values of p/p_s and are given in Table 1. A graph was drawn for the relation of V/V_m to p/p_s, and with the aid of this graph, using the single-point method, we calculated the specific surfaces of catalysts whose surface areas had been previously calculated from isotherms in earlier investigations [1, 6]. A comparison of the results is made in Table 2.

In addition, we measured the specific surfaces of some catalysts based on alumina. The calculations were made by the BET equation and by Equation 2. Some of these results are given in Table 3, in Fig. 3, and in Table 4. The determinations based on a single measurement of equilibrium were carried out at p/p_s = = about 0.1. Apart from these quantities (S determined from the BET equation or from the point B on the isotherm, and S_T determined by the single-point method), values of ΔS and the departure of S_T from S expressed as a percentage are given in Tables 2 and 4. These results show that in twenty-two out of

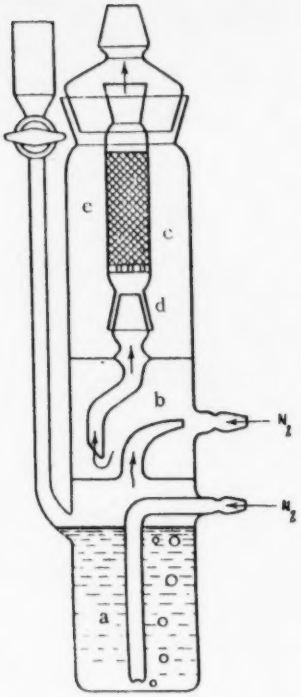

Fig. 2.

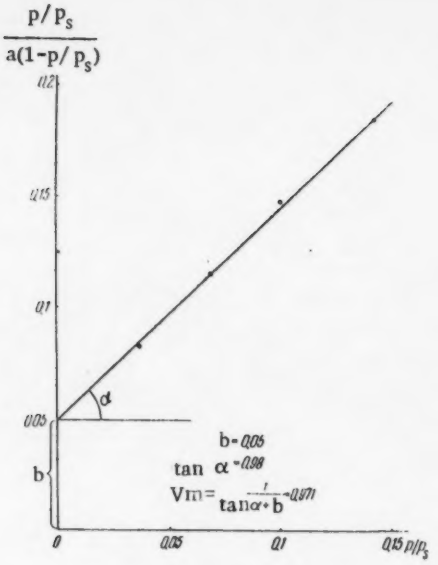

Fig. 3.

TABLE 1

p/p_s	V/V_m
0.053	0.570
0.069	0.655
0.100	0.770
0.122	0.850
0.181	1.000

TABLE 2

No.	Catalyst	p/p_s	S_T (sq.m/g)	S (sq.m/g)	ΔS (%)
1	SiO_2	0.100	520	550	— 5.5
2	MgO — 33	0.100	202	200	1.0
3	MgO — 32	0.100	172	176	— 2.5
4	MgO — 30	0.100	182	179	1.7
5	MgO — Mg phosphate	0.100	165	157	5.0
6	MgO — Mg phosphate	0.118	140	124	13.0
7	MgO — 12	0.118	121	110	10.0
8	MgO — Mg phosphate	0.100	110	113	— 2.6
9	MgO — NiO	0.100	94	103	— 6.8
10	MgO — MnO	0.100	94	89	5.6
11	MgO — CdO	0.100	51	47	8.5
12	MgO — 36	0.100	23	28	—18.0
13	MgO — 39	0.100	22	22	0
14	Ni Se	0.100	30	23	30.0
15	Ni Se — ZnSe	0.100	33	35	— 5.7
16	MgO — 11	0.100	11.5	12	— 4.2
17	MgO — 14	0.100	10	10	0
18	MgO — 37	0.100	8	11	—26.0

TABLE 3

Weighed Portion 1.4822 g

Calculation by the BET equation						Calculation by single-point method
p/p_s	weight increase (g)	a (mm/g)	$1-p/p_s$	$a(1-p/p_s)$	$\frac{p/p_s}{a(1-p/p_s)}$	
0.036	0.0515	0.444	0.964	0.428	0.084	$p/p_s = 0{,}100$
0.069	0.0734	0.634	0.931	0.590	0.117	$V/V_m = 0{,}77$
0.100	0.0851	0.735	0.900	0.662	0.151	(from graph)
0.142	0.1018	0.880	0.858	0.755	0.188	For $p/p_s = 0{,}100$ $V = 0.735$, whence $V_m = 0.954$
S = 228 sq.m/g (see Fig. 3)						S = 225 sq.m/g

TABLE 4

$p/p_s = 0.100$

No.	Catalyst	S_T (sq.m/g)	S (sq.m/g)	ΔS (%)
	Calcined			
1	Al_2O_3 — ZnO. at 400°	225	228	1.3
2	Al_2O_3 — ZnO. " 750°. № 1	70	97	—28
3	Al_2O_3 — ZnO. " 600°	181	183	— 1.1
4	Al_2O_3 — ZnO. " 750°. № 2	120	130	— 7.7
5	Al_2O_3 — CdO. " 600°	106	112	— 5.4
6	Al_2O_3 — CdO. " 750°	137	150	— 8.7
7	Al_2O_3 — ZnO	120	140	—14.3
8	Al_2O_3, № 1	284	284	0
9	Al_2O_3, № 2	442	470	6.0
10	Al_2O_3 — UO_3	59	56	— 5.4

twenty-eight determinations S_T differed from S by less than 10 % and only in six determinations was the difference greater — it then attained 30% but it is possible that Catalyst 14 (Table 2) was oxidized during the determination (the high increase in weight and the result). It should be noted that high percentage errors were associated mainly with catalysts of low specific surface.

On the basis of this investigation we consider that calculation by Temkin's method (Equation 2) gives quite satisfactory results not only for the standard procedure in the low-temperature adsorption of nitrogen, but also for the determination of equilibrium under the conditions of adsorption of benzene vapor from a stream of carrier gas at ordinary pressure. The latter method opens up great possibilities for multiple and routine determinations because of the simplicity of the apparatus used: it may be useful in the elucidation of the changes occurring in a catalyst during thermal treatment, during long periods of use, during poisoning and regeneration, etc.

In conclusion, we may remark that we made several calculations by the aid of the equation proposed by Katz [3] (Equation 1), and we found that, when applied to adsorption data obtained under flow conditions, it gave very great departures of S_T from S.

SUMMARY

1. It was shown that the equation proposed by Temkin for the determination of specific surfaces of

catalysts from a single measurement of adsorption equilibrium gives good results not only in the low-temperature adsorption of nitrogen, but also in the adsorption of benzene vapor at room temperature and atmospheric pressure in a flow system. Such measurements must be made at a relative pressure in the region of 0.1.

2. A new apparatus is described for the determination of adsorption under flow conditions.

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OPTICAL METHOD OF INVESTIGATING HYDROCARBONS

COMMUNICATION 10. RAMAN SPECTRA OF SOME NAPHTHENES

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A. F. Plate, and E. M. Terentyeva

This paper forms a continuation of a series of papers [1-9] describing investigations of the Raman spectra of hydrocarbons carried out jointly by the Optical Laboratory of the P. N. Lebedev Physical Institute and the N. D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR. Results are now given for nine naphthene hydrocarbons and one aromatic hydrocarbon.

EXPERIMENTAL

All measurements were made with a Zeiss spectrograph having a camera of f = 270 mm and aperture = = f/4.5. Frequencies and intensities were measured as in previous investigations [3].

Results of Measurements

The measured values of frequencies and intensities are given below. The method of preparation is described briefly for each hydrocarbon, and its principal constants (boiling point, density, refractive index) are given. In the present paper intensities are expressed on a somewhat modified scale, which was established in the way indicated previously [10]. The characteristics of the lines are denoted as follows: b - broad; sh - sharp; bk - the line stands on a background of appreciable intensity; db - double; (?) - possibly a repeat from another exciting frequency.

1 - Cyclopentylhexane. Reaction of 3-chlorocyclopentene with hexylmagnesium bromide gave 1-(2-cyclopenten-1-yl) hexane, which was hydrogenated in the cold in presence of palladium black. The resulting hydrocarbon was purified by chromatography on silica gel and by vacuum distillation through a 25-plate column. 1- Cyclopentylhexane had b.p. 81.5° (12mm); n_D^{20} 1.4395; d_4^{20} 0.7966; found MR 50.96; calculated for $C_{11}H_{22}$ MR 50.80. The literature [11] gives b.p. 203° (760 mm); n_D^{20} 1.4392; d_4^{20} 0.7965.

$\Delta\nu$: 238 (17); 262 (13, b), 417 (0, b), 784 (0,b), 802 (2), 838 (5, b), 859 (12, b), 892 (28), 943 (0), 966 (0,b), 1010 (4, b), 1024 (11), 1050 (2), 1066 (8), 1084 (8), 1099 (5), 1131 (12), 1169 (2, b), 1202 (0), 1248 (0,b), 1281 (0, b), 1304 (17), 1341 (2), 1358 (1, b), 1384 ? (1, b), 1437 (60), 1452 (60), 1479 (4), 2660 (0), 2712 (5, b), 2737 (5, b), 2851 (210), 2872 (220), 2895 (200, bk), 2911 (180, bk), 2937 (200), 2962 (160).

1 - Cyclopentylheptane. Reaction of 3-chlorocyclopentene with heptylmagnesium bromide gave 1-(2-cyclopenten-1-yl) heptane, which was hydrogenated in the cold without solvent in presence of platinized charcoal activated with palladium chloride solution. The product was steam-distilled and then distilled through a 25-plate column. It was then purified chromatographically on silica gel. 1-Cyclopentylheptane had b. p. 225.1 – 225.2° (760 mm). n_D^{20} 1.4420; d_4^{20} 0.8010; found MR 55.56; calculated for $C_{12}H_{24}$ MR 55.42. The literature [11] gives b. p. 224.0° (760 mm); n_D^{20} 1.4421; d_4^{20} 0.8010.

$\Delta\nu$: 222 (7), 247 (7 b), 770 (0), 847 (4, b), 867 (11, b), 894 (23), 952 (3, b), 1011 (5, b), 1026 (13), 1065 (10), 1082 (10), 1097 (10), 1132 (8), 1173 (2,b), 1198 (0, b), 1250 (0,b), 1304 (26), 1346 (3), 1439 (75), 1449 (75), 1474 (3, b), 2853 (230), 2877 (220), 2905 (220), 2937 (250), 2961 (210).

1- Cyclopentyloctane. Reaction of 3-chlorocyclopentene with octylmagnesium bromide gave 1-(2-cyclopenten-1-yl) octane, which was hydrogenated in presence of palladium black in the cold. The product was distilled and purified chromatographically on silica gel. It was redistilled through a 25-plate column. 1-Cyclopentyloctane had b. p. 113.7° (10 mm); n_D^{20} 1.4444; d_4^{20} 0.8047; found MR: 60.39; calculated for $C_{13}H_{26}$ MR 60.03. The literature [11] gives b. p. 243° (760 mm); n_D^{20} 1.4446; d_4^{20} 0.8048.

$\Delta\nu$: 205 (0), 237 (5,b), 260 (3, b), 370 (0, b), 410 (0, b), 510 (0, b), 605 (0, b), 759 (0), 795 (0, b), 839? (0), 852 (5), 871 (3), 894 (23), 922 (0), 947 (0), 967 (1), 994 (0), 1021 (12), 1033 (12), 1063 (11), 1082 (11), 1100 (11), 1131 (11), 1167 (0), 1190 (0), 1215 (0), 1254 (0), 1281 (0), 1304 (24, b), 1320 (0), 1347 (0), 1370 (0), 1440 (55), 1451 (55), 1480 (3), 2660 (0), 2724 (0), 2853 (230), 2871 (230, bk), 2894 (250, bk), 2938 (200, bk), 2964 (160).

Bicyclohexyl. This was prepared by hydrogenating repeatedly recrystallized biphenyl in presence of Raney nickel at 200° and 150 atm. The product was distilled from a flask fitted with a Vigreux column and had b. p. 237.2 – 237.7° (760 mm) n_D^{20} 1.4795; d_4^{20} 0.8845; found MR 53.34; calculated for $C_{12}H_{22}$ MR 53.22. The literature [12] gives b. p. 238 – 239° (760 mm); n_D^{20} 1.4795; d_4^{20} 0.8848.

$\Delta\nu$: 249 (13), 275 (42), 362 (3, b. db), 434 (19), 461 (12), 484 (10), 514 (8), 656 (3), 767 (41), 787 (30), 799 (14), 847 (45), 895 (3, b), 926 (3, b), 956 (6), 1038 (110), 1053 (7), 1082 (17), 1108 (9), 1139 (7), 1162 (11), 1177 (7), 1193 (16), 1206 (11, b), 1238 (20), 1250 (20), 1267 (75), 1297 (11), 1351 (42), 1444 (150), 1465 (7), 2659 (6, b), 2679 (3), 2748 (7), 2850 (760, b), 2892 (250), 2923 (660), 2940 (670).

Dicyclohexylmethane. This was prepared by hydrogenating repeatedly recrystallized diphenylmethane in presence of Raney nickel at 120° and 100 atm. The product was distilled from a flask fitted with a Vigreux column and had b. p. 96.5° (3 mm); n_D^{20} 1.4762; d_4^{20} 0.8773; found MR 57.95; calculated for $C_{13}H_{24}$ MR 57.83. The literature [13] gives b. p. 250 – 252°; n_D^{20} 1.4752; d_4^{20} 0.8750.

$\Delta\mu$: 231 (7, b), 258 (39), 415 (0), 424 (12), 444 (19), 474 (4, b), 553 (3), 767 (17), 784 (38), 794 (65), 842 (44), 1034 (110), 1047 (40), 1065 (6), 1088 (11), 1107 (10, b), 1145 (4, b), 1186 (13, db), 1210 (12), 1262 (110), 1275 (19, b), 1302 (17), 1350 (33), 1368 (16), 1445 (150), 1466 (10), 2848 (460), 2858 (460), 2885 (220), 2902 (220), 2923 (500), 2934 (400).

1,2 - Dicyclohexylethane. This was prepared from carefully purified diphenylethane by hydrogenation in presence of Raney nickel at 180-245° and 125 atm. The product was purified chromatographically on silica gel and was then distilled under reduced pressure through a 30-plate column; it then had m. p. + 11.35°; b. p. 127.8° (9 mm); n_D^{20} 1.4758; d_4^{20} 0.8742; found MR 62.83; calculated for $C_{14}H_{26}$ MR 62.45.

Our product appeared to be appreciably purer than the preparations described in the literature.

$\Delta\nu$: 195 (27), 202 (25), 261 (13, b), 337 (1), 393 (0), 435 (21), 445 (21), 469 (0), 535 (2), 549 (2), 582 (5), 638 (0), 779 (35, b), 798 (80), 842 (35), 860 (0), 889 (4), 911 (4), 933 (2), 971? (14), 1032 (110), 1053 (25), 1082 (17), 1103 (11, b), 1160 (12), 1180 (12), 1201? (12), 1235 (2), 1263 (80), 1294 (20), 1346 (29), 1365 (18), 1443 (140), 1463 (9), 2670 (10, b), 2739 (2), 2848 (470), 2893 (50, bk), 2918 (370), 2938 (360).

cis - Decahydronaphthalene. The mixture of isomers was first freed from naphtahlene and tetrahydronaphthalene impurity by chromatographic adsorption on silica gel, and the cis isomer was isolated by vacuum fractionation through a 25-plate column. It had b. p. 70.0° (12 mm); n_D^{20} 1.4810; d_4^{20} 0.8962; found MR 43.90; calculated for $C_{10}H_{18}$ MR 43.98. The literature [11] gives b. p. 195.69° (760 mm); n_D^{20} 1.4810, d_4^{20} 0.8965.

$\Delta\nu$: 320 (16), 355 (16), 378 (27), 444 (8), 513 (2), 597 (70), 745 (100), 796 (23), 835 (11), 852 (40), 888 (3), 932 (10), 972 (14), 982 (27), 1013 (28), 1043 (110), 1073 (28), 1089 (14), 1110 (3, b), 1143 (2), 1167 (13), 1219 (14), 1244 (75), 1270 (60), 1309 (0), 1332 (8, b), 1345 (27, b), 1444 (100, b), 1466 (23), 2856 (430), 2863 (430), 2895 (290), 2920 (520), 2934 (530, b).

trans - Decahydronaphthalene. Commercial decalin was treated with aluminum chloride at room temperature for 12 hours, treated chromatographically for the removal of naphthalene and tetrahydronaphthalene, distilled through a 35-plate column, and again purified chromatographically. It had b. p. 187.3° (760 mm);

n_D^{20} 1.4687; d_4^{20} 0.8697; found MR 44.21; calculated for $C_{10}H_{18}$ MR 43.98. The literature [11] gives b. p. 187.25° (760 mm); n_D^{20} 1.4695; d_4^{20} 0.8699.

It is possible that the preparation so obtained contained a trace of cis-decahydronaphthalene.

$\Delta\nu$: 304 (13, b), 408 (150), 494 (110), 564 (5), 755 (80), 849 (50), 878 (24), 904 (2), 933 (1), 994 (29, b), 1058 (140), 1090 (2), 1141 (14), 1162 (43), 1232 (40), 1256 (120), 1349 (20), 1365 (65), 1448 (130), 1460 (20, b), 2660 (12), 2691 (2), 2831 (480, b), 2853 (530), 2891 (250), 2916 (540), 2935 (620).

Hexahydroindan. This was prepared by the hydrogenation of indan in presence of Raney nickel at 200° and 140 atm. The product was treated with concentrated sulfuric acid and distilled through a 30-plate column. As we did not succeed in isolating the stereoisomers in the completely pure state, we studied one fraction, which probably contained a predominance of trans-hexahydroindan and had b. p. 162.0 – 163.5° (760 mm); n_D^{20} 1.4630; d_4^{20} 0.8601; found MR 39.78; calculated for C_9H_{16} MR 39.36. The literature [14] gives: cis-hexahydroindan – b. p. 166° (760 mm); n_D^{20} 1.4713; d_4^{20} 0.8815; trans-hexahydroindan – b. p. 159 – 160° (760 mm); n_D^{20} 1.4638; d_4^{20} 0.8630.

$\Delta\nu$: 242 (0,b), 301 (3), 327 (6), 411 (8), 424 (33), 471 (7), 497 (32), 526 (1), 572 (7, b), 669 (2, b), 750 (3), 768 (28), 776 (27), 804 (6), 839 (10), 853 (6), 891 (25), 907 (10), 930 (9), 973 (5), 1000 (8), 1029 (10, b), 1044 (25), 1054 (20), 1078 (7, b, db), 1126 (9), 1159 (3), 1189 (8, b, db), 1244 (10, b), 1263 (14), 1297 (4), 1311 (3), 1340 (13), 1367 (17), 1447 (95), 1468 (8, b), 2662 (3, b), 2722 (5), 2852 (270), 2887 (190), 2923 (500), 2932 (650), 2957 (220).

Indan. This was prepared by the hydrogenation of indene in an autoclave at room temperature in presence of Raney nickel. The product was distilled through a 30-plate column. It had b. p. 177.2 – 177.4° 760 mm); n_D^{20} 1.5383; d_4^{20} 0.9640; found; MR 38.36; calculated for C_9H_{10} MR 37.96. The literature [12] gives b. p. 177.5 – 178.5° (760 mm); n_D^{20} 1.5383; d_4^{20} 0.9639.

$\Delta\nu$: 197 (130, b, bk), 236 (8, b, bk), 258 (8, b, bk), 419 (6), 520 (180), 584 (55), 605 (0), 740 (75), 756 (65), 835 (8, b), 856 (75), 908 (37), 998 (28), 1026 (310), 1106 (1, b), 1156 (43, b), 1180 (4), 1204 (90), 1220 (41), 1271 (27, db), 1322 (40), 1439 (130), 1459 (18), 1585 (44), 1607 (55), 2845 (190), 2866 (14), 2892 (190), 2913 (120), 2952 (240, b), 3022 (8), 3043 (270), 3072 (130).

Discussion of Experimental Results

In earlier papers of this series we have given the spectra of monosubstituted cyclopentanes from methyl- to pentyl-cyclopentane [3]. To these results we can now add data for three more hydrocarbons, hexyl-, heptyl-, and octyl-cyclopentanes. Comparison of the spectra studied in the paper [3] with those studied in the present investigation enables us to establish certain patterns of behavior.

The spectra of monosubstituted cyclopentanes contain many weak and diffuse lines. In this series of hydrocarbons most of the frequencies coincide; as a rule, the differences are to be found in the region 150-600 cm^{-1}. The most intense deformation line, which occurs in this region, moves with increase in the size of the radical in the direction of lower frequencies (from 534 cm^{-1} (18) in methylcyclopentane to 237 cm^{-1} (5) in 1-cyclopentyloctane). All these spectra contain also the line 890 cm^{-1}, which is attributable to the fully symmetrical vibration of the cyclopentane ring. It is of interest to follow the changes in the intensity at the maximum, expressed on an equimolecular basis, for the given vibration of monosubstituted hydrocarbons. This is shown in the table, from which it will be seen that the molecular intensity of the line of frequency 890 cm^{-1} is approximately constant. The same table gives the intensities of the 1305 cm^{-1} line, which is attributable to vibrations of CH_2 groups.

It was to be expected that the intensity of the 1305 cm^{-1} line would increase with lengthening of the chain, i.e. with increase in the number of CH_2 groups, and this is actually observed. A reduction in intensity in the case of ethylcyclopentane may be caused by an error in the estimation of the intensity, as in this case the intensity was estimated visually. Increase in intensity with increase in the number of CH_2 groups in the molecule occurs also for the line 1445 cm^{-1}, but the changes in intensity are distorted by the superposition of the neighboring line at 1455 cm^{-1}.

TABLE

$\Delta\nu$ (cm^{-1})	Structural formula							
890	49	37	38	47	46	54	48	52
1305	6	2	10	19	24	33	55	55

We investigated the following bicyclic hydrocarbons: bicyclohexyl, dicyclohexylmethane, and 1,2-dicyclohexylethane. Our results for bicyclohexyl agree closely with those obtained by Han and Matsuno [15] with respect both to frequencies and to the distribution of intensities within the spectrum. There is a noteworthy resemblance of the spectra of the bicyclic hydrocarbons among themselves and to the monosubstituted cyclohexanes [3].

Many papers have appeared on the investigation of cis- and trans-decahydronaphthalenes [16-18], but most authors have investigated a mixture of the two forms. The purest preparations were those of Rank [18], who investigated them by a photoelectric method. Comparison of our results with those of Rank shows that in a number of lines there are discrepancies in frequency of 6-8 cm^{-1}. These discrepancies are probably due to errors in the photoelectric method. The distribution of intensities within the spectrum agrees qualitatively with our results. We made a careful spectroscopic investigation of our preparations for extraneous impurities and admixture of one form with the other. It was established that naphthalene and tetrahydronaphthalene were absent in both forms.

The spectrum of the trans form contains fewer lines owing to the presence of a center of symmetry in the molecule and to "alternative exclusion," and its lines are sharp and intense. The spectrum of the cis form contains more lines, and the lines are less intense. Although they have many lines in common, the spectra of the cis and trans forms contain a number of fairly intense lines that can be used for distinguishing the one from the other. Such lines are the following:

for cis-decahydronaphthalene (cm^{-1}): 378 (27), 597 (70), 1043 (110)
for trans-decahydronaphthalene (cm^{-1}): 408 (150), 494 (110), 1058 (140)

These lines enable us to estimate the amount of one form present in the other. The spectroscopic results showed that each of the preparations was adequately purified from the other isomer; if any of the other isomer was present, then it was in a proportion of less than one percent.

Our spectrum results for indan and hexahydroindan are in fairly close agreement with the results of other authors [19-21] with respect both to frequencies and to the distribution of intensities within the spectrum.

Dicyclohexylmethane was prepared by M. Yu. Lukina, dicyclohexylethane by E. A. Mikhailova, and cis-decahydronaphthalene by O. D. Sterligov, and the authors are greatly indebted to these workers.

SUMMARY

1. Raman spectra are given for three monocyclic cyclopentane hydrocarbons, three bicyclic cyclohexane hydrocarbons, and four bicyclic hydrocarbons having condensed rings. All intensities at the maxima were determined photometrically.

2. It was confirmed for the case of C_{11}—C_{13} hydrocarbons that the intensity per molecule of the line at 890 cm^{-1} is approximately constant for monosubstituted cyclopentane hydrocarbons.

3. A resemblance was noted of the spectra of bicyclohexyl, dicyclohexylmethane, and 1,2-dicyclohexylethane between themselves and to the spectra of monosubstituted cyclohexane hydrocarbons.

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EXCHANGE REACTIONS OF ZIRCONIUM TETRAKISACETYLACETONATE

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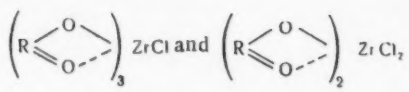
Chelate zirconium compounds have received very little study. Several chelate compounds of zirconium with β-diketones are known in which zirconium exhibits a coordination number of eight. Some of these were prepared by Biltz's method [1] by reaction of β-diketones with a zirconium salt in aqueous solution in presence of sodium carbonate, and others were obtained by the process of two-phase extraction [2, 3]. The reactions of these compounds have not been investigated. A few other chelate zirconium compounds have been described [4, 5]; they may be prepared, for example, by reaction of phenylglycolic acid with zirconyl chloride. A Coordination number of six is represented by a few halides of the type (I) and (II) [6-8]. They were synthesized by reaction of β-diketones, hydroxy ketones, hydroxy aldehydes, hydroxy acids, and hydroxy esters with zirconium tetrachloride in nonaqueous solvents.



(I) (II)

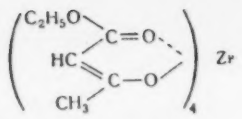
Zirconium trisacetylacetonate chloride can be converted into the decahydrate of zirconium tetrakisacetylacetonate by the action of acetylacetone in presence of water and sodium carbonate [6]. Zirconium trisdibenzoylmethane chloride can be converted into zirconium trisacetylacetonate chloride by the action of excess of acetylacetone under anhydrous conditions [6]. These methods, however, are not general. Thus, negative results were obtained in attempts to apply Biltz's method to homologs of acetylacetone and to benzoylacetone [6], and also in attempts to prepare chelate zirconium compounds of coordination number eight by the direct action of zirconium tetrachloride on compounds such as benzoylacetone and salicylaldehyde [6, 8].

The present paper describes a study of the exchange reactions of zirconium tetrakisacetylacetonate, one of the most readily available chelate compounds. It was of interest to examine the possibility of passing from zirconium tetrakisacetylacetonate to other, less accessible eight-coordinated chelate zirconium compounds. It was of interest also to study the possibility of passing to six-coordinated zirconium compounds and also to alkyl orthozirconates.

By reaction between zirconium tetrakisacetylacetonate and benzoylacetone we succeeded in replacing residues of one β-diketone by residues of another and so obtained zirconium tetrakisbenzoylacetonate. As stated above, attempts to prepare this compound by other methods have not been successful.

Reaction between zirconium tetrakisacetylacetonate and salicylaldehyde proceeds with formation of the chelate compound $(OC_6H_4CHO)_4Zr$ for which another method of preparation failed [8]. This product is a solid substance, sparingly soluble in organic solvents and readily forming stable complexes, for example, the double compound with one molecule of chloroform $(OC_6H_4CHO)_4\ Zr \cdot CHCl_3$.

Reaction of acetoacetic ester with zirconium tetrakisacetylacetonate gives a compound of the following composition:



This compound is a viscous liquid which can be distilled in a high vacuum.

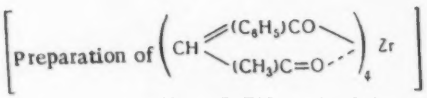
Zirconium tetrakisacetylacetonate and tetrakisbenzoylacetonate readily react with acetyl chloride with formation of the corresponding zirconium chlorides. These compounds are described in the literature, and in this case the method of passing from eight-coordinated chelate zirconium compounds to six-coordinated compounds is of some interest. Zirconium trisbenzoylacetonate chloride was prepared also by reaction of zirconium trisacetylacetonate chloride with benzoylacetone.

By reaction of zirconium tetrakisacetylacetonate with excess of butyl and benzyl alcohols, butyl and benzyl orthozirconates were prepared. It was thus found possible to pass from chelate zirconium compounds to simple orthozirconic esters.

EXPERIMENTAL

The experiments were carried out with dry reactants and with exclusion of atmospheric moisture.

Reaction of Zirconium Tetrakisacetylacetonate With Benzoylacetone

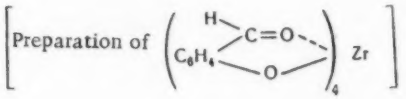


A mixture of 4.87 g (0.01 mole) of zirconium tetrakisacetylacetonate and 6.48 g (0.04 mole) of benzoylacetone was heated to 100°. A clear melt was obtained, and at 20-25 mm and 100° acetylacetone slowly distilled off. The yield was quantitative. The solid residue was purified by crystallization from benzene. The product melted at 200-202°. It was poorly soluble in benzene; somewhat better in dioxane.

Found %: C 65.38; 65.40; H 5.20; 5.05;
Zr 12.32; 12.18

$(C_{10}H_9O_2)_4$ Zr. Calculated %: C 65.26; H 4.93;
Zr 12.40

Action of Salicylaldehyde on Zirconium Tetrakisacetylacetonate



A solution of 5 g of zirconium tetrakisacetylacetonate in 30 ml of salicylaldehyde was heated in a vacuum to remove acetylacetone. As acetylacetone distilled off, a yellow precipitate separated from the reaction mixture. A further 30 ml of salicylaldehyde was added, and the operation was continued. The precipitate (5.5 g) was filtered off, washed with petroleum ether, and dried in a current of dry air. The product was almost insoluble in hot petroleum ether and in hot diethyl ether; it was sparingly soluble in dioxane and benzene; and it was somewhat more highly soluble in salicylaldehyde, chloroform, and dichloroethane. After recrystallization from salicylaldehyde, it melted at 204-206°.

Found %: C 61.82; 61.59; H 3.86; 3.88;
Zr 12.38; 12.19

$(OC_6H_4CHO)_4Zr \cdot 1.5\ OHC_6H_4CHO$. Calculated %: C 60.90; H 3.85; Zr 12.13

In another experiment the crude product was recrystallized from chloroform. This substance melted at 210-212°.

Found %: C 50.44; 50.30; H 2.96; 3.31;
Cl 15.01; 14.85; Zr 13.04; 12.98;

$(OC_6H_4CHO)_4 \cdot Zr \cdot CHCl_3$. Calculated %: C 50.09; H 3.04; Zr 13.13; Cl 15.30

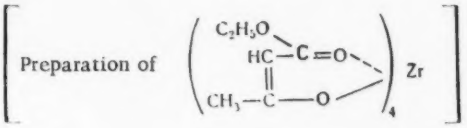
Only after long heating at 50-60° and $2 \cdot 10^{-3}$ mm did the compound cease to contain chloroform.

Found %: C 58.52; 58.65; H 3.30; 3.26;
Zr 16.14; 15.66;

$(OC_6H_4CHO)_4$ Zr. Calculated %: C 58.40; H 3.50; Zr 15.86

The product then formed a light-yellow powder, m.p. 207-210°.

Action of Acetoacetic Ester on Zirconium Tetrakisacetylacetonate

Preparation of 

Acetoacetic ester (40 ml) was added to zirconium tetrakisacetylacetonate (5 g). A mixture of acetylacetone and acetoacetic ester was distilled off at 40 mm and 90-100°. The operation was repeated until the acetylacetone and excess of acetoacetic ester had been removed. The total duration of reaction was 8-10 hours. The yield was almost quantitative. The viscous residue was distilled at $8 \cdot 10^{-3}$ mm.

Found %: C 47.52; 47.53; H 5.74; 5.63;
Zr 15.20; 15.15;

$(C_6H_9O_3)_4$ Zr. Calculated %: C 47.45; H 5.97; Zr 15.03

Action of Acetyl Chloride on Zirconium Tetrakisacetylacetonate

[Preparation of Zirconium Trisacetylacetonate Chloride]

A solution of 1.56 g (0.02 mole) of acetyl chloride in benzene was added to a solution of 9.74 g (0.02 mole) of zirconium tetrakisacetylacetonate in benzene. The reaction mixture was heated for two hours at 95-100°. Solvent was distilled off, and the solid residue was crystallized from benzene. The yield was 5.8 g (68 %).

Found %: C 42.41; 42.62; H 4.87; 4.81;
Zr 21.65; 21.47; Cl 8.55; 8.54

$(C_5H_7O_2)_3$ ZrCl. Calculated %: C 42.55; H 4.96; Zr 21.40; Cl 8.38

The zirconium trisacetylacetonate chloride prepared in this way melted at 155-157°. Its molecular weight was determined cryoscopically in benzene:

Found : M 447; 445

$(C_5H_7O_2)_3$ Zr Cl. Calculated : M 423.8

It should be noted that the zirconium trisacetylacetonate chloride that we prepared by the method given in the literature [6], i.e. reaction between acetylacetone and zirconium tetrachloride, also melted at 156-157°, whereas the literature gives m. p. 100-101° for this monochloride.

Reaction of Zirconium Tetrakisbenzoylacetonate with Acetyl Chloride

[Preparation of Zirconium Trisbenzoylacetonate Chloride]

A solution of 0.23 g (0.003 mole) of acetyl chloride in 5 ml of benzene was added gradually to a cooled solution of 2.18 g (0.003 mole) of zirconium tetrakisbenzoylacetonate in 15 ml of benzene. The reaction mixture was heated for 2.5 hours, and solvent was then distilled from the clear liquid. The residue was recrystallized three times from benzene. After the second and third recrystallizations the product melted at 146-147.5°. The yield of purified product was 0.95 g (50%). For zirconium trisbenzoylacetonate chloride the literature [6] gives m.p. 126-127°.

Found %: C 59.13; 59.34; H 4.57; 4.51;
Zr 14.64; 14.75; Cl 5.61; 5.32

$(C_{10}H_9O_2)_3Zr$. Calculated %: C 59.03; H 4.46; Zr 14.96; Cl 5.81

Reaction of Zirconium Trisacetylacetonate Chloride with Benzoylacetone

[Preparation of $(C_{10}H_9O_2)_3ZrCl$]

Zirconium trisacetylacetonate chloride (2.12 g, i.e. 0.005 mole) was added to 2.43 g (0.015 mole) of benzoylacetone. The reaction mixture was heated to 110°. Acetylacetone was distilled under reduced pressure from the clear melt. The residue was recrystallized three times from benzene. After the second and third recrystallizations the product melted at 145.5-147.5°. The yield of purified product was 1.58 g (50%).

Found %: C 59.39; 59.35; H 4.52; 4.61; Zr 14.65; 14.75; Cl 5.71

Butyl Orthozirconate $(C_4H_9O)_4Zr$

A solution of 4.87 g of zirconium tetrakisacetylacetonate in 30 ml of butyl alcohol was heated for 30 minutes at 115-117°, and a mixture of acetylacetone and butyl alcohol was slowly distilled off until there was no longer a reaction for acetylacetone in the distillate (test with $FeCl_3$). The operation was repeated until a test for acetylacetone in the reaction mixture was negative. Excess of butyl alcohol was distilled off a 10^{-4} mm. The total duration of the reaction was 10-12 hours. The yield of crude product was 3.52 g (about 92%).

The resulting butyl orthozirconate was distilled at $1.5 \cdot 10^{-3}$ mm.

Found %: C 49.81; 49.80; H 9.36; 9.29;
Zr 23.91; 23.60

$(C_4H_9O)_4$ Zr. Calculated %: C 49.65; H 9.46; Zr 23.79

Benzyl Orthozirconate $(C_6H_5CH_2O)_4Zr$

A solution of 5.3 g of zirconium tetrakisacetylacetonate in 30 ml of benzyl alcohol was heated under reduced pressure (40 mm), and a mixture of acetylacetone and benzyl alcohol slowly distilled off. The operation was repeated until the reaction mixture ceased to give a reaction for acetylacetone (test with $FeCl_3$), and benzyl alcohol was then distilled off under reduced pressure. The resulting viscous product was dissolved in

petroleum ether. Suspended matter was filtered off, solvent was distilled off, and the residue was heated at 0.5 mm and 120-140° for two hours to remove volatile substances. The yield was 5 g (89%). The undistilled product was analyzed.

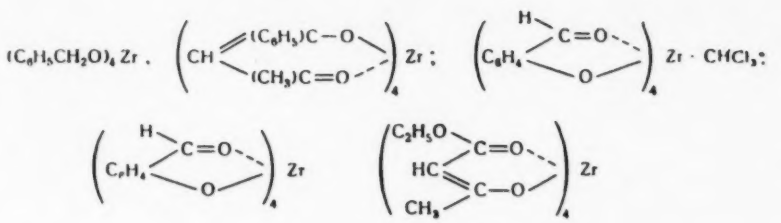
Found %: C 64.29; 64.35; H 5.49; 5.46;
Zr 17.57; 17.32
$(C_6H_5CH_2O)_4Zr$. Calculated %: C 64.69; H 5.43; Zr 17.50

Benzyl orthozirconate is a very viscous liquid which decomposes when distilled ($2 \cdot 10^{-4}$ mm) with formation of benzyl alcohol and polymer.

SUMMARY

1. On the basis of a study of the reaction of zirconium tetrakisacetylactonate under anhydrous conditions with butyl and benzyl alcohols, benzoylacetone, salicylaldehyde, and acetoacetic ester it was shown that chelate groups of one sort can be completely replaced by chelate groups of a different sort and also by alkoxy and benzyloxy groups.

2. By this method the syntheses were performed of butyl orthozirconate and the following previously undescribed compounds:



3. Reaction between equimolecular proportions of zirconium tetrakisacetylacetonate and acetyl chloride gave zirconium trisacetylacetonate chloride $(C_5H_7O_2)_3ZrCl$ and similarly, zirconium tetrakisbenzoylacetonate gave zirconium trisbenzoylacetonate chloride $(C_{10}H_9O_2)_3ZrCl$.

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REACTIONS OF CHLOROACETYL CHLORIDE, TRICHLOROACETYL CHLORIDE, AND PHOSGENE WITH TRIALKYL PHOSPHITES

M. I. Kabachnik and P. A. Rossiiskaya

Some years ago, while studying the formation of α-keto phosphonic esters from acid halides and trialkyl phosphites [1], we came across cases in which the reaction was anomalous and gave isomeric products that did not contain keto groups. We had shown previously that acid chlorides generally react smoothly with trialkyl phosphites with formation of α-keto phosphonic esters, the reaction proceeding with rearrangement of the Arbuzov type:

$$RCOCl + P(OR')_3 \rightarrow RCOPO(OR')_2 + R'Cl \quad (I)$$

α-Keto phosphonic esters enter into reactions for carbonyl which are given only by compounds containing very active carbonyl groups [2]. Thus, they not only very readily form hydrazones and semicarbazones in an acid medium, but they also combine with sodium bisulfite, give readily crystallizing hemiacetals with alcohols, and can be hydrolyzed with decomposition of the haloform type. It was quite natural to conclude that the enhanced activity of the carbonyl group, as compared with the carbonyl of ketones, is due to the effect of the neighboring phosphonic grouping. We considered that it would be interesting to prepare substances with a still more active carbonyl group, in which the group would occur between two phosphonic groupings or between a phosphonic grouping and a chlorine-containing group. For the synthesis of substances containing such arrangements of atoms we wished to apply the reactions of trialkyl phosphites with acid chlorides derived from chloride-containing acids (chloroacetic, trichloroacetic) and with phosgene. These reactions, it was considered, should proceed as follows:

$$CH_2ClCOCl + 2P(OR)_3 \rightarrow (RO)_2P(O)-CH_2-COP(O)(OR)_2 \quad (II)$$

$$CCl_3COCl + 2P(OR)_3 \rightarrow (RO)_2P(O)-CCl_2-COP(O)(OR)_2 \quad (III)$$

$$COCl_2 + 2P(OR)_3 \rightarrow (RO)_2P(O)-CO-P(O)(OR)_2 \quad (IV)$$

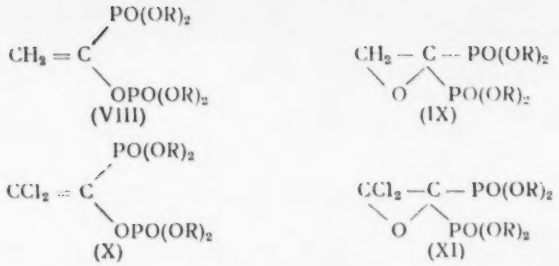
However, unexpected results were obtained.

Phosgene reacted smoothly with trimethyl phosphite in accordance with the Arbuzov scheme, methyl chloride being liberated and dimethyl (chloroformyl) phosphonate formed:

$$COCl_2 + P(OCH_3)_3 \rightarrow ClCOP(O)(OCH_3)_2 + CH_3Cl \quad (V)$$

When a second molecule of the phosphorous ester reacted with the (chloroformyl) phosphonic ester, Arbuzov rearrangement again occurred with formation of tetramethyl carbonyldiphosphonate (VI):

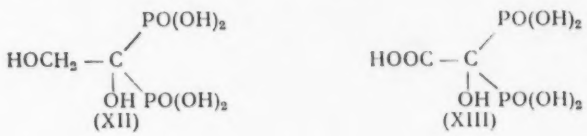
$$ClCOP(OCH_3)_2 + P(OCH_3)_3 \rightarrow (CH_3O)_2PCOP(OCH_3)_2$$
$$\quad\quad\quad



(VIII) (IX)

(X) (XI)

When hydrolyzed, (VIII) and (X) should decompose with formation of acetic and dichloroacetic acids, respectively, together with phosphoric and phosphorous acids. On the other hand, (IX) and (XI) should give the hydroxy diphosphonic acids (XII) and (XIII), which, generally speaking, are compounds of a more stable type:



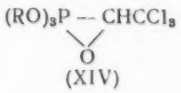
(XII) (XIII)

However, if, owing to the heavy load of electronegative radicals on the central carbon atom, hydrolytic elimination of one phosphonic grouping occurs in the form of phosphoric acid, then a keto phosphonic acid will be formed intermediately and will decompose with formation of a molecule of phosphorous acid. The result of acid hydrolysis will then be the same as in the case of (VIII) and (X). Hence, the question of the structure of the reaction products remained open, a fact that prevented us from publishing the above-described results.

Recently, Perkow [4] showed that halo aldehydes react with trialkyl phosphites not in accordance with the Arbuzov rearrangement [5], but with formation of halovinyl esters of phosphoric acid:

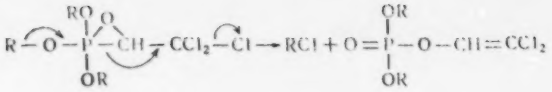
$$P(OR)_3 + CHOCCl_3 \rightarrow (RO)_2POCH{=}CCl_2 + RCl$$
$$\|$$
$$O$$

Later, American investigators [6-8] and Pudovik and Lebedeva [9] confirmed this for a large number of cases: α-chloro aldehydes and ketones, in reacting with trialkyl phosphites, depart from the usual scheme of the Arbuzov rearrangement and attach themselves to phosphorus not through carbon, but through oxygen. It is supposed that an intermediary in the reaction is the α-epoxide (XIV):



(XIV)

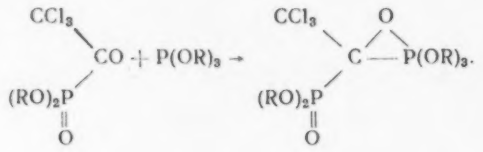
Other possibilities have been considered. In the light of these results it becomes clear that the structures of the products of the reaction of trialkyl phosphites with chloroacetyl chloride and with trichloroacetyl chloride are (VIII) and (X). As regards the mechanism of the reaction, the suggestion of the American authors [7] must be regarded as very probable: the trialkyl phosphite molecule is attacked by chloral in such a way that the most electrophilic atom of the aldehyde molecule – the carbonyl carbon – attaches itself to phosphorus with formation of the α-epoxide (XIV). We suppose that this intermediary (XIV) then decomposes as a result of changes in the system of conjugated single bonds:



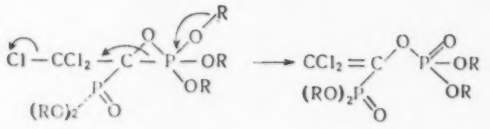
In the reaction of trichloroacetyl chloride with trialkyl phosphite, in the first stage normal Arbuzov rearrangement occurs:

$$CCl_3COCl + P(OR)_3 \rightarrow CCl_3COPO(OR)_2$$

In the resulting trichloroacetylphosphonic ester the most electrophilic atom is the carbon of the highly active carbonyl group, which combines with another molecule of phosphorous ester:



Elimination of RCl gives the final Product:



EXPERIMENTAL

Dimethyl (Chloroformyl) phosphonate (V). A current of dry phosgene was passed into 37.2 g of trimethyl phosphite with cooling; there was a copious evolution of methyl chloride. When reaction was complete (theoretical increase of weight, disappearance of odor of phosphorous ester), the reaction mixture was warmed to 50° and carbon dioxide was passed. Two vacuum fractionations gave 32.0 g (61.8 %) of a clear colorless liquid, b.p. 66-67° (11 mm); d_4^{20} 1.3282; n_D^{20} 1.4116; found MR 32.29; calculated MR 32.16

Found %: P 18.07; 17.80 $C_3H_6O_4PCl$. Calculated %: P 17.98

Tetramethyl Carbonyldiphosphonate (VI). A mixture of 32.0 g of dimethyl (chloroformyl) phosphonate and 23.1 g of trimethyl phosphite was heated under reflux for four hours in a water bath and then 90 minutes in an oil bath at 140°. During the reaction, carbon dioxide was passed through the mixture. When reaction was complete (disappearance of the odor of phosphorous ester), the mixture was heated in a vacuum at 100° for 30 minutes and then fractionated. The product, amounting to 22.2 g (48.7%), boiled at 126° (2 mm). With repeated distillation the substance decomposed; d_4^{20} 1.3365; n_D^{20} 1.4252; found MR 47.08; calculated MR 47.03

Found %: P 25.12 $C_5H_{12}O_7P_2$. Calculated %: P 25.20

Hydrate of Tetramethyl Carbonyldiphosphonate (VII). To 1.81 g of tetramethyl carbonyldiphosphonate, the equivalent amount of water (0.14 g) was added. After 36 hours the mixture thickened. When vacuum-distilled, the whole came over at 141-142° (1 mm). Redistillation did not affect the boiling point; d_4^{20} 1.3080; n_D^{20} 1.4140; found MR 50.43; calculated MR 50.07.

Found %: P 23.40; 23.41. $C_5H_{14}O_8P_2$. Calculated %: P 23.50

Action of Chloroacetyl Chloride on Trimethyl Phosphite (Preparation of (VIII, R = CH_3). Trimethyl phosphite (30.3 g, i.c., 0.244 mole) was added gradually to ice-cooled chloroacetyl chloride (13.8 g, i.c., 0.122 mole). Methyl chloride was evolved. The mixture was set aside overnight and then vacuum-fractionated. The product, amounting to 27.0 g (85.5%), was a clear colorless liquid, soluble in water and alcohol, and having b.p. 128-130°, d_4^{20} 1.3194; n_D^{20} 1.4400; found MR 51.93; calculated MR 52.31

Found %: C 27.61; 27.77; H 5.26; 5.32; P 23.74; 23.81
$C_6H_{14}O_7P_2$. Calculated %: C 27.70; H 5.38; P 23.86

The substance did not give a color with ferric chloride, and it did not react with sodium bisulfite, p-nitrophenylhydrazine, semicarbazide, or sodium.

Hydrolysis of the Substance (VIII, R = CH_3). The substance (1.1223 g) was refluxed over a gauze for 15 hours with 20 ml of 1:1 hydrochloric acid. The solution was then diluted with water to 100 ml. In 10 ml of this solution phosphoric acid was determined by precipitation with magnesia mixture, which gave 0.0449 g of $Mg_2P_2O_7$; P^V found, 11.15%; P^V calculated for the elimination of one phosphonic grouping, 11.93%.

The mother liquor from the determination of phosphoric acid was evaporated, acidified with hydrochloric acid, and precipitated with mercuric chloride; 0.1783 g of calomel was obtained; P found, 10.42%; P calculated for the elimination of one phosphonic grouping, 11.93%.

Reaction of Chloroacetyl Chloride with Triethyl Phosphite (Preparation of VIII, R = C_2H_5). Triethyl phosphite (33.2 g, i.e., 0.2 mole) was added gradually to 11.3 g (0.1 mole) of chloroacetyl chloride, the mixture being cooled externally so that the temperature did not rise above 30°. Ethyl chloride was evolved. After removal of residual ethyl chloride in a vacuum at 40°, the reaction product was distilled at 1.5 mm. Two fractionations gave 14.9 g of a substance of b.p. 132 – 135°; d_4^{20} 1.1820; n_D^{20} 1.4402; found MR 70.49; calculated MR 70.78

Found %: C 38.05; 37.90; H 6.99; 6.77; P 20.25; 19.95
$C_{10}H_{22}P_2O_7$. Calculated %: C 37.98; H 6.96; P 19.63

The product was a clear colorless liquid, readily soluble in water, alcohol, chloroform, and ether.

Action of Trichloroacetyl Chloride on Trimethyl Phosphite (Preparation of X, R = CH_3). To 18.7 g of trichloroacetyl chloride, cooled with a mixture of ice and salt, 24.3 g of trimethyl phosphite was added gradually. Fractionation gave 17.1 g (53.0%) of a substance of b.p. 155-156° (1.5 mm). It was a colorless liquid, insoluble in water, but soluble in alcohol; d_4^{20} 1.4914; n_D^{20} 1.4710; found MR 61.66; calculated MR 62.04

Found %: C 21.83; 21.78; H 3.80; 3.78; P 19.05; 19.08; Cl 21.57
$C_6H_{12}O_7P_2Cl_2$. Calculated %: C 21.89; H 3.65; P 18.81; Cl 21.56

Hydrolysis of the Substance (X, R = CH_3). The substance (0.6238 g) was heated over a gauze for ten hours with 20 ml of 1:1 hydrochloric acid. The solution was then diluted with water to 50 ml, and 10 ml of this was precipitated with mercuric chloride; 0.1688 g of calomel was obtained; P^{III} found, 8.88%; P^{III} calculated for the elimination of one phosphonic grouping, 9.43%. The mother liquor from the determination of phosphorous acid was acidified with nitric acid, and phosphorus was determined as magnesium pyrophosphate in the usual way: 0.0417 g of $Mg_2P_2O_7$; P^V found 9.31%; P^V calculated, 9.43%.

SUMMARY

1. It was shown that phosgene reacts with two molecules of a trialkyl phosphite with rearrangement of the Arbuzov type.

2. Chloroacetyl chloride and trichloroacetyl chloride react with trialkyl phosphites with formation of substituted vinyl esters of phosphoric acid.

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β-KETO PHOSPHONIC ESTERS

COMMUNICATION 1. PHOSPHONOACETIC AND ACETONYLPHOSPHONIC ESTERS, AND THEIR HOMOLOGS

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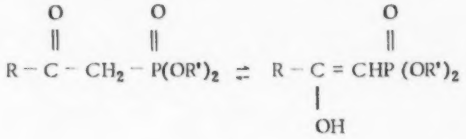
In a brief communicaton [1] we outlined our work on the synthesis of β-keto phosphonic esters with the view of studying the possible tautomerism of compounds of this type.

As Arbuzov showed [2], there is a close analogy between carboxy and phosphono groups. In phosphonoacetic esters, as in malonic esters, hydrogen of the methylene group may be replaced by metal. The phosphorus analog of ethyl acetoacetate – diethyl acetonylphosphonate, synthesized by Razumov and Petrov [3] – and that of ethyl benzoylacetate – diethyl phenacylphosphonate, synthesized by Arbuzov and Razumov [4] – react with sodium. Kosolapoff [5] showed that the hydrogen of the methylene group of tetraethyl methylenediphosphonate is replaceable by metal. Other properties of derivatives of β-keto phosphonic acids also point to their similarity of β-keto carboxylic acids [6].

All these results point to the possibility of tautomerism in β-keto phosphonic esters [4, 7]:



No direct evidence is to be found in the literature on the existence of enol forms – not to mention the proportions in which they are present – in β- keto phosphonic esters and in malonic ester analogs (phosphonoacetic esters).

With the object of examining the question of the existence of enol forms of β-keto phosphonic esters and comparing the relative effects of carboxy and phosphono groups on the tendency for the formation of enol forms, in 1949 we began work on the synthesis of the necessary phosphorus compounds and their study by chemical and physical methods.

In the present communication we report results on the synthesis of some derivatives of phosphonoacetic ester, and also of acetonylphosphonic ester and its methyl derivatives, and on the titration of these compounds with bromine. At first it appeared that the question of the occurrence of keto-enol tautomerism could be readily resolved by the use of Meyer's classical method of titration with bromine and by comparison of the absorption spectra of unsubstituted and monosubstituted derivatives of β-keto phosphonic esters with the spectra of disubstituted derivatives, for which tautomerism is impossible. Our investigations showed, however, that for the phosphorus analogs of acetoacetic ester and other β-keto carboxylic esters the picture is considerably more complex.

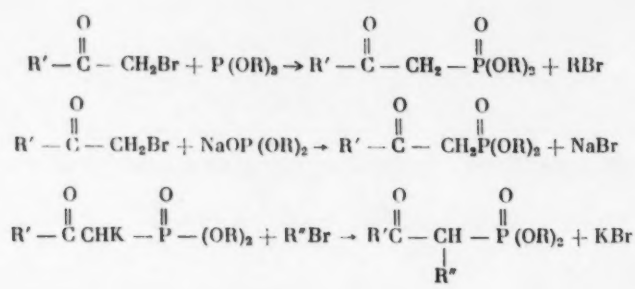
The following methods can be used for the synthesis of the compounds required:

Method A – Action of α-halo carbonyl compounds on phosphorous esters (Arbuzov rearrangement).

Method B – Action of sodium dialkyl phosphites on α-halo carbonyl compounds (Michaelis-Becker

reaction).

Method C – For substituted derivatives, alkylation of metal derivatives of β-phosphono carbonyl compounds with alkyl halides.



(A)

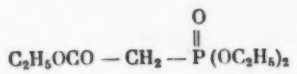
(B)

(C)

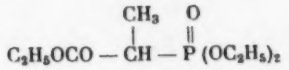
It would appear that syntheses by Methods A, B, and C should give the same products. However, as will be shown below, the constants and properties of substances prepared by different methods differ considerably.

We synthesized the previously prepared analogs of malonic ester – phosphonoacetic, 2-phosphonopropionic, and 2-methyl-2-phosphonopropionic esters – and they were titrated with bromine by Meyer's classical method in which 2-naphthol is used [8]. We checked the possibility of applying the Meyer method of bromination to compounds of the type of phosphono carboxylic esters in the case of 3-phosphonopropionic ester, which did not react with bromine under our titration conditions.

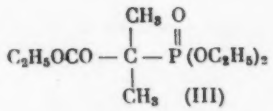
Triethyl phosphonoacetate (I) (prepared by Methods A and B), triethyl 2-phosphonopropionate (II) (prepared by Method C), and triethyl 2-methyl-2-phosphonopropionate (III) (prepared by Method C) did not react with bromine, which indicated the absence of any determinable amounts of enol form in phosphonoacetic and 2-phosphonopropionic esters. 2-Methyl-2-phosphonopropionic ester cannot, of course, exist in an enol form.



(I)



(II)



(III)

There is therefore an analogy between phosphonoacetic and malonic esters, for it has not been found possible, either, to detect any enol form in the latter. The infrared spectrum shows [9] that in presence of sodium ethoxide, malonic ester forms enolate ions only to the extent of 30-35 %, whereas, under the same conditions, β-keto esters give 95-100 % of enolate ions.

Considerable interest is presented by the study of acetonylphosphonic esters and their derivatives, which are analogs of acetoacetic ester. Diethyl acetonylphosphonate was synthesized by the action of triethyl phosphite on bromoacetone, and the 1-methyl- and 1, 1-dimethyl-acetonyl phosphonates were synthesized by the action of triethyl phosphite on 3-bromo-2-butanone and 3-bromo-3-methyl-2-butanone, respectively. By the action of triethyl phosphite on 1-bromo-2-butanone, diethyl 2-oxobutylphosphonate was obtained.

Table 1 gives the results of the titration of the products with bromine by Meyer's method (removal of excess of bromine with 2-naphthol). For comparison, data on the enol contents (determined by the same method) of the corresponding carboxylic esters are given.

TABLE 1

No.	Substance	amount of enol (%)	Substance	Unsaturation, expressed as enol content (%)
1	$CH_3CO-CH_2COOC_2H_5$	7.5	$CH_3CO-CH_2-P(=O)-(OC_2H_5)_2$	1.1
2	$CH_3CH_2CO-CH(CH_3)-COOC_2H_5$	—	$CH_3CH_2-CO-CH(CH_3)-P(=O)-(OC_2H_5)_2$	5.0
3	$CH_3-CO-CH(CH_3)-COOC_2H_5$	4	$CH_3-CO-CH(CH_3)-P(=O)-(OC_2H_5)_2$	Ca 9.0*
4	$CH_3-CO-C(CH_3)=C(CH_3)-OC_2H_5$	0	$CH_3-CO-C(CH_3)_2-P(=O)-(OC_2H_5)_2$	23

* Titration with bromine did not give reproducible results.

A comparison of the data in Table 1 indicates that no analogy exists between the bromine-titration results for the phosphonic and the carboxylic compounds. For acetoacetic and acetonylphosphonic esters the difference was not marked, but it was surprising to find that diethyl 1, 1-dimethylacetonylphosphonate, which is incapable of enolization, showed considerable unsaturation (23 %).

Perkow [10] recently showed that reaction of chloral with trialkyl phosphites proceeds anomalously and results in the formation of unsaturated phosphoric esters:

$$CCl_3-CHO + P(OR)_3 \rightarrow CCl_2=CH-O-P(=O)(OR)_2 + RCl.$$

In 1954, while our investigations were in progress, Pudovik [11] showed that this anomalous reaction may occur also with α-halo ketones, the normal product being accompanied by an unsaturated phosphoric ester:

$$RCO-CH_2Br + P(OR')_3 \rightarrow \begin{cases} R-CO-CH_2-P(=O)-(OR')_2 \\ R-C(=CH_2)-O-P(=O)-(OR')_2 \end{cases} + R'Br.$$

The amount of phosphoric ester formed depends on reaction temperature and on the identity of the halogen compound. High temperature favors the formation of the keto phosphonic ester, and low temperature favors the phosphoric ester. Chloro compounds sometimes give almost exclusively the unsaturated phosphoric ester. The formation of unsaturated phosphoric esters provides also the explanation of anomalous cases of unsaturation in the disubstituted derivatives. In other cases, however, the enol content found by the bromine-titration method could be explained by the presence of small amounts of difficultly removable unsaturated phosphoric ester.

In order to determine the cause of the unsaturation of acetonylphosphonic ester and its derivatives, we prepared these compounds not only by Method A (action of triethyl phosphite on the corresponding ketones),

but also by Method B (action of sodium diethyl phosphite on bromo ketones) and by Method C (alkylation of the potassium derivative of acetonylphosphonic ester). As will be seen from Table 2, the preparations obtained by Methods A, B, and C differed in their constants.

TABLE 2

Substance	Method	B.p. in °C (p in mm)		d_0^{20}	n_D^{20}	Unsaturation (%)
Diethyl acetonyl phosphonate *	A	99—102	(1.5)	1.1232	1.4355	1.1
	A	137	(13)	1.1420	1.4365	1.0
	B	99—100	(1.5)	1.1574	1.4400	1.1
	B	106—106.5	(8.5)	1.1127	1.4332	1.8
Diethyl isopropenyl phosphate	A	107.5—109	(18)	1.0757	1.4200	81.0
Diethyl 2-oxobutyl-phosphonate	A	99—100	(0.5)	1.0917	1.4360	5.0
Diethyl 1-methyl-acetonylphosphonate**	A	92	(0.5)	1.0820	1.4342	Ca 9.0
" "	B	108.5—109	(5.5)	1.0863	1.4350	3.0
	C	115—116.5	(6.0)	1.0815	1.4368	1.0
Diethyl "isobutenyl" phosphate**	A	112—113.5	(10)	1.0602	1.4270	73.0
Diethyl 1,1-dimethyl-acetonylphosphonate	A	112—112.5	(8)	1.0515	1.4360	21.0
	B	103—103.5	(5)	1.0592	1.4360	2.0
	C	114	(8)	1.0645	1.4380	0.4

* See spectra in Fig. 3.

** The compound listed in a previous paper ([1], Table 1, No. 5) as diethyl 1-methylacetonylphosphonate has been found to be the isomeric diethyl "isobutenyl" phosphate.

Publisher's Note: "Isobutenyl" has been used in Russian literature both in the meaning of "2-methylallyl" and also in the meaning of "2-methylpropenyl"; here, however, it would appear to mean "1-methylpropenyl".

It will be seen from Table 2 that compounds obtained by the action of sodium diethyl phosphite on bromo ketones have somewhat lower boiling points than compounds obtained by the action of triethyl phosphite and by alkylation.

Judging by the titration results, the 1,1-dimethylacetonylphosphonic ester prepared by Method A contains a considerable amount of the unsaturated phosphoric ester. Attempts to remove unsaturated ester by transesterification with ethanol were not successful. The degree of unsaturation remained high (15%).

These results clearly do not enable us to resolve the question of the presence of enolic forms and their amounts in diethyl acetonylphosphonate and its methyl derivative. The question demands further study by chemical and physical methods.

We studied also the ultraviolet absorption spectra of the compounds synthesized. The results have been given previously in a brief communication [12]. However, the differences in the constants and absorption spectra of substances prepared by isomerization and by reaction with sodium diethyl phosphite remained obscure. In the present communication we give some preliminary results obtained with the object of elucidating this matter.

Treatment of 3-bromo-2-butanone with triethyl phosphite gave two compounds: one of b.p. 112-113.5° (10mm), which showed 73% unsaturation in the titration with bromine (diethyl "isobutenyl" phosphate – see Publisher's Note to Table 2), and one of b.p. 92° (0.5 mm) having about 9% unsaturation (diethyl 1-methylacetonylphosphonate). Figure 1 gives the absorption spectra of alcoholic solution of diethyl 1-methylacetonylphosphonate and diethyl 2-oxobutylphosphonate prepared by Method A, and also the spectrum of diethyl 1-methylacetonylphosphonate prepared by the methylation of the potassium derivative of diethyl acetonylphosphonate, which

is very close to that of diethyl acetonylphosphonate (Method A). In a solution of sodium methoxide or hydroxide diethyl 1-methylacetonylphosphonate (Methods A and C) gives increased absorption in the region of 2400 A, behavior which is analogous to that of diethyl acetonylphosphonate and diethyl 2-oxobutylphosphonate under the same conditions [12].

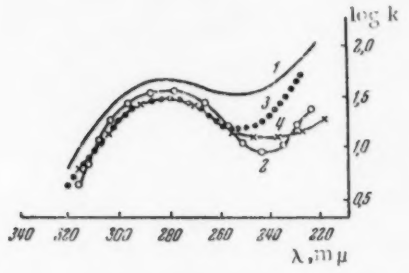


Fig. 1. Absorption spectra in methanol solution:
1) diethyl 1-methylacetonylphosphonate (Method C);
2) diethyl 2-oxobutylphosphonate (Method A);
3) diethyl acetonylphosphonate (Method A);
4) diethyl 1-methylacetonylphosphonate (Method A)

Titration in alkaline solution with bromine by Grossmann's procedure [13] gave 72.1% unsaturation (expressed as enol content) for diethyl 2-oxobutylphosphonate. Titration of the same ester in absolute alcohol in presence of sodium ethoxide gave 164% unsaturation. The position is therefore close to that of acetoacetic ester, for which titration in absolute alcohol in presence of sodium ethoxide gives 131% of enol [14].

The absorption spectrum of diethyl "isobutenyl" phosphate is given in Fig. 2, in which, for comparison, absorption curves are given for diethyl isopropenyl phosphate and diethyl vinyl phosphate, prepared by Upson [15]. As will be seen, diethyl "isobutenyl" phosphate has a somewhat different absorption spectrum without characteristic maxima. In the case of the diethyl vinyl ester there is a very flat maximum in the region of 2500 A.

One of the sources of the difference in the absorption spectra of acetonylphosphonic ester preparations obtained from triethyl phosphite and from sodium diethyl phosphite may be the presence of traces of dimethylaniline in the original phosphorous ester. Halmann [16] showed that results obtained for the absorption spectra of phosphorous esters by Milobedzki and Borowsky [17] and by de Hauss [18]* are incorrect, since the phosphorous ester contained dimethylaniline used for binding hydrogen chloride; this caused absorption in the neighborhood of 2510 A and 1990 A [19].

The dimethylaniline of its hydrochloride that is present in triethyl phosphite may pass further into diethyl acetonylphosphonate. To check this possibility, triethyl phosphite was prepared by the action of sodium ethoxide on phosphorus trichloride and was then converted into diethyl acetonylphosphonate, which had the following constants: b.p. 137° (13 mm); d_0^{20}, 1.1420; n_D^{20} 1.4365. Diethyl acetonylphosphonate prepared from triethyl phosphite with the aid of triethylamine as acid-binding agent had b.p. 99 – 100° (1.5 mm); d_0^{20}, 1.1574 and n_D^{20} 1.4400 [20] and differed appreciably in constants from the above preparation and particularly from the product obtained with the aid of dimethylaniline, which had b.p. 99 – 102° (1.5 mm); d_0^{20} 1.1232; n_D^{20} 1.4355 [1].

The spectrum of the diethyl acetonylphosphonate obtained from triethyl phosphite prepared with the aid of the ethoxide had an absorption maximum at 2800 A and had a spectrum identical with that of the preparation obtained with the aid of triethylamine (Fig. 3). The spectrum of the diethyl acetonylphosphonate prepared from phosphorous ester obtained with the aid of dimethylaniline had a maximum not only at 2800 A, but also at 2500 A, at which there was a minimum in the other cases (Fig. 3). The spectrum of diethyl isopropenyl phosphate has an analogous maximum at 2500 A of the same intensity (Fig. 2).

When titrated with bromine, diethyl acetonylphosphonate samples prepared from phosphorous esters prepared in different ways all showed insignificant contents of unsaturated compounds. As this was true for the preparation obtained with the aid of dimethylaniline, the absorption at 2500 A must evidently be attributed rather to traces of dimethylaniline than to the unsaturated phosphoric ester.

We made attempts to prepare the diethyl and ethylene acetals of diethyl acetonylphosphonate with the object of obtaining the acetonylphosphonic ester in the pure state by the hydrolysis of these acetals, but they

* The contents of de Hauss's paper are very surprising, for it repeats – literally and down to the last figure – the material given in the paper by Milobedzki and Borowski without making any reference to this paper.

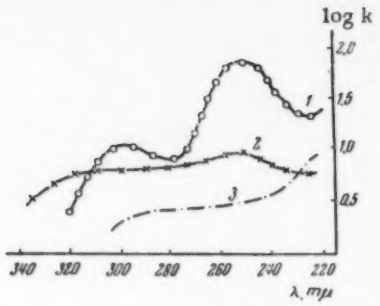


Fig. 2. Absorption spectra in methanol solution: 1) diethyl isopropenyl phosphate; 2) diethyl vinyl phosphate; 3) diethyl "isobutenyl" phosphate.

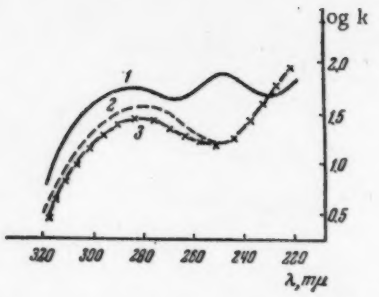


Fig. 3. Absorption spectra in methanol solution of diethyl acetonylphosphonate prepared by Method A from triethyl phosphite synthesized 1) with the aid of dimethylaniline; 2) from $C_2H_5ONa + PCl_3$; 3) with the aid of triethylamine.

were unsuccessful. There was no reaction when the diethyl acetal of bromoacetone was heated with triethyl phosphite at 195°, and the cyclic ethylene acetal of bromoacetone did not react with sodium diethyl phosphite.

EXPERIMENTAL

1. Triethyl Phosphonoacetate was prepared by the action of sodium diethyl phosphite on ethyl chloroacetate in absolute alcohol: b.p. 143 – 144° (11 mm); n_D^{20} 1.4310; d_0^{20} 1.1215; found MR 51.75; calculated MR 51.66. Meyer titration with bromine gave 0% unsaturation.

2. Triethyl 2-Phosphonopropionate was prepared in two ways. a) Methylation of the potassium derivative of triethyl phosphonoacetate with methyl iodide: b.p. 136.5 – 137.5° (10 mm); n_D^{20} 1.4310; d_0^{20} 1.0930; found MR 56.42; calculated MR 56.28. Titration with bromine gave 0% unsaturation.

b) Action of triethyl phosphite on ethyl 2-bromopropionate: the latter was dropped into the former at 140°, and ethyl bromide distilled off; the bath temperature was 170-190° when addition was complete. Yield 75%; b.p. 137 – 138.5° (17 mm); n_D^{20} 1.4315; d_0^{20} 1.0960; found MR 56.43.

3. Triethyl 2-Methyl-2-phosphonopropionate was prepared [21] by the action of methyl iodide on the potassium derivative of triethyl 2-phosphonopropionate prepared by Method C (see 2a, above) in an ether medium: b.p. 128 – 128.5° (8 mm); 103 – 103.5° (1 mm); n_D^{20} 1.4310; d_0^{20} 1.0774; found MR 60.62; calculated MR 60.30. Titration with bromine gave 0% unsaturation.

Attempts to prepare triethyl 2-methyl-2-phosphonopropionate by the action of ethyl 2-bromo-2-methylpropionate on triethyl phosphite were unsuccessful. The reaction did not go at a bath temperature of 190°, and at 210-230° in sealed tubes resinification occurred.

An experiment was carried out also on the reaction between ethyl 2-bromo-2-methylpropionate and potassium diethyl phosphite. No triethyl 2-methyl-2-phosphonopropionate could be isolated from the products, and the constants of the product isolated differed from those of triethyl 2-methyl-2-phosphonopropionate.

Potassium diethyl phosphite was prepared from 8.6 g of potassium, 30.4 g of diethyl hydrogen phosphite, and 10.1 g of absolute ethanol in 250 ml of dry ether (reaction was completed by heating on the water bath for 40 minutes). Ethyl 2-bromo-2-methylpropionate (43 g) was added dropwise to the resulting salt, and vigorous reaction occurred with evolution of heat. Potassium bromide (30 g) was filtered off, ether was distilled off, and the residue was vacuum-distilled. A fraction (28 g) was obtained having b.p. 79 – 80° (2 mm); n_D^{20} 1.4050; d_0^{20} 1.0633. Redistillation gave a product having b.p. 97.5 – 98° (12 mm); n_D^{20} 1.4060; d_0^{20} 1.0684

Found %: P 16.53; 16.91 $C_{10}H_{21}O_4P$. Calculated %: P 13.13

4. Diethyl Acetonylphosphonate was prepared in two ways.

a) Treatment of triethyl phosphite with bromoacetone. Triethyl phosphite (50 g) prepared with the aid of triethylamine was dropped into bromoacetone (41 g) heated to 120°. Ethyl bromide distilled off (30 g; theory requires 33 g). Fractionation gave a fraction of b.p. 42-98° (2mm) and 40 g of a fraction of b.p. 98-109° (3 mm). Fractionation of the lower fraction gave 2 g of a substance of b.p. 57-59.5° (3.5 mm) and n_D^{20} 1.4150 and 3 g of diethyl isopropenyl phosphate, b.p. 77-80° (3 mm) and n_D^{20} 1.4228. Fractionation of the fraction of b.p. 98-109° (3 mm) through a Widmer column gave diethyl acetonylphosphonate, b.p. 99 – 100° (1.5 mm); n_D^{20} 1.4400; d_0^{20} 1.1574; found MR 44.23; calculated MR 45.40. Titration with bromine gave 1.1% unsaturation. The 2,4-dinitrophenylhydrazone of diethyl acetonylphosphonate was prepared. * 2,4-Dinitrophenylhydrazine (0.5 g) was dissolved by warming it with 1-1.5 ml of concentrated sulfuric acid and adding 7 ml of alcohol.

An alcoholic solutions of 0.5 g of diethyl acetonylphosphonate was added to the freshly prepared reagent. No precipitate formed, and water was added dropwise until a turbidity appeared. Yellow crystals formed after a time; they were washed with alcohol and then melted at 86-90°. After recrystallization from alcohol they melted at 105-106°, and the melting point did not change after further recrystallization. Dawson and Burger [22] give m.p. 124-125.5°.

Found %: P 8.62 $C_{13}H_{19}O_7N_4$. Calculated %: P 8.29

When triethyl phosphite prepared with the aid of dimethylaniline was used, the diethyl acetonylphosphonate obtained had the following constants: b.p. 99 – 102° (1.5 mm); n_D^{20} 1.4355; d_0^{20} 1.1232. Triethyl phosphite prepared by the action of sodium ethoxide on phosphorus trichloride gave diethyl acetonylphosphonate having b.p. 137° (13 mm); n_D^{20} 1.4365; d_0^{20} 1.1420.

b) Treatment of sodium diethyl phosphite with bromoacetone. Sodium diethyl phosphite was prepared from 10.5 g of sodium in 350 ml of ligroin (b.p. 80-120°) and 60 g of diethyl hydrogen phosphite. The resulting solution was added to 60 g of bromoacetone diluted with ligroin; heat was evolved. When reaction was complete, the mixture was refluxed for 90 minutes. Ligroin was distilled off, and repeated fractionation through a Widmer column gave 16 g of a fraction of b.p. 106 – 106.5° (8.5 mm); n_D^{20} 1.4332; d_0^{20} 1.1127; found MR 45.38; calculated MR 45.40. Titration with bromine gave 1.8% unsaturation.

Found %: P 15.65; 15.83 $C_7H_{15}O_4P$. Calculated %: P 15.97

No dinitrophenylhydrazone could be obtained under the conditions described above; unchanged dinitrophenylhydrazine sulfate was recovered.

5. Diethyl Isopropenyl Phosphate was prepared by Pudovik's method [11] by the action of triethyl phosphite on chloroacetone: b.p. 107.5 – 109° (18 mm); n_D^{20} 1.4200; d_0^{20} 1.0557, found MR 45.68; calculated MR 46.05.

Titration with bromine gave 81% unsaturation.

6. Diethyl 1-Methylacetonylphosphonate was prepared in three ways.

a) Action of triethyl phosphite on 3-bromo-2-butanone. 2-Butanone was brominated as described in [23]. Reaction was between 120 g of the ketone and 160 g of bromine in presence of 250 ml of water and 30 g of potassium chlorate. Fractionation through a Widmer column gave 84.5 g of 3-bromo-2-butanone, b.p. 50-51.5° (28 mm), and 26.5 g of 1-bromo-2-butanone, b.p. 67.5-69.5° (29 mm). 3-Bromo-2-butanone (27 g) was added dropwise to 29 g of triethyl phosphite at 150°; 14.5 g of ethyl bromide distilled off (theoretical amount 17.5 g). Fractionation through a Widmer column gave fractions of b.p. 112-120° (9.5 mm) and 124-130° (9.5 mm). On standing, the higher fraction turned pink. Two fractionations of the lower fraction gave 13.5 g (37%) of a fraction of b.p. 112 – 113.5° (10 mm); n_D^{20} 1.4270; d_0^{20} 1.0602; found MR 50.41; calculated for $C_8H_{17}O_4P$ MR 50.67.

Found %: P 14.82 $C_8H_{17}O_4P$. Calculated %: P 14.89

Distillation of the higher fraction gave 8 g of a substance having b. p. 92° (0.5 mm); n_D^{20} 1.4342; d_0^{20} 1.0820; found MR 50.14; calculated MR 50.02

* Work on the preparation of dinitrophenylhydrazones was carried out by N. A. Polezhaeva.

Found %: P 15.04; 15.12 $C_8H_{17}O_4P$. Calculated %: P 14.89

b) Action of sodium diethyl phosphite on 3-bromo-2-butanone. Sodium diethyl phosphite was prepared from 42 g of diethyl hydrogen phosphite and 7 g of sodium in ethereal solution. The solution of sodium diethyl phosphite was added to 45 g of 3-bromo-2-butanone diluted with ether. Heat was evolved, and the ether boiled gently. Reaction was completed in a water bath for 90 minutes. Sodium bromide isolated amounted to 35 g. Fractionation gave:

Fraction I, b.p. up to 112° (10 mm); 1.5 g, mainly 3-bromo-2-butanone
Fraction II, b. p. 112 – 114° (10 mm); 45 g
Fraction III, b.p. 114 – 130° (10 mm); 4 g
Fraction IV, b.p. 130 – 155° (8 mm)

Fractionation of Fraction II through a Widmer column gave a fraction of b.p. 108 – 110° (8 mm); n_D^{20} 1.4350; d_0^{20} 1.0863; found MR 50.01; calculated MR 50.02. Titration with bromine gave 3.0% unsaturation.

Found %: P 15.05; 14.80 $C_8H_{17}O_4P$. Calculated %: P 14.89

c) Methylation of diethyl acetonylphosphonate. Finely cut potassium (3.8 g) was introduced into 100 ml of dry dioxane, and gradual addition was made of 19 g of diethyl acetonylphosphonate (prepared by the action of triethyl phosphite on bromoacetone). The potassium reacted vigorously, and a clear solution was obtained. Excess of methyl iodide (20 g; the theoretical amount is 13.9 g) was added to the solution. The temperature rose, and potassium iodide was precipitated. Reaction was completed in a water bath (1 hour). The mixture was centrifuged, dioxane was distilled off, and the residue was fractionated. A fraction (12 g) of b.p. 127-129° (12 mm) was obtained. Fractionation through a Widmer column gave a fraction having b.p. 120 – 121° (7.5 mm); 115 – 116.5° (6 mm); n_D^{20} 1.4368; d_0^{20} 1.0815; found MR 50.40; calculated MR 50.02. Titration with bromine gave 0.9% unsaturation.

Found %: P 14.72 $C_8H_{17}O_4P$. Calculated %: P 14.89

7. Diethyl 1,1-Dimethylacetonylphosphonate was prepared in three ways.

a) Action of triethyl phosphite on 3-bromo-3-methyl-2-butanone. 3-Bromo-3-methyl-2-butanone was prepared as follows: 2-methyl-3-butyn-2-ol has hydrated to 3-hydroxy-3-methyl-2-butanone [24], and treatment of this with phosphorus tribromide gave 3-bromo-3-methyl-2-butanone. Phosphorus tribromide was added very cautiously to the hydroxy ketone, reaction being vigorous. When addition was complete, the mixture was heated in a water bath for 20 minutes. It was poured into water, and ether extraction, washing with 5% sodium carbonate solution, drying with calcium chloride, and distillation gave the bromo ketone, b.p. 41 – 42° (18 mm); n_D^{14} 1.4578.

Triethyl phosphite (27 g) was added dropwise to 27 g of the bromo ketone, which was first heated to 140° in a distilling flask. Ethyl bromide began to be liberated at a bath temperature of 150°; 14 g was distilled off. Toward the end of the reaction the bath temperature was raised to 190°. Fractionation gave Fraction I, b.p. up to 100° (7 mm), and Fraction II, b.p. 100-104° (5 mm). A substance of b.p. 71-73° (10 mm) and n_D^{19} 1.4210, was isolated from Fraction I. Distillation of Fraction II through a Widmer column gave a fraction of b.p. 112 – 112.5° (8 mm); n_D^{20} 1.4360; d_0^{20} 1.0515; found MR 55.0 calculated MR 54.64. Titration with bromine gave 21% unsaturation.

An attempt to remove admixed unsaturated ester by transesterification was unsuccessful. A mixture of 13 g of diethyl 1,1-dimethylacetonylphosphonate, 15 ml of absolute alcohol, and a very small amount of sodium was taken, and alcohol was carefully distilled off. Fractionation through a Widmer column gave a fraction having b.p. 107-110° (20 mm), n_D^{20} 1.4103; d_0^{20} 1.0623 (triethyl phosphite) and a fraction having b.p. 123 – 125° (17 mm); n_D^{20} 1.4300; d_0^{20} 1.0518; found MR 54.59. Titration of the fraction with bromine gave 15.4% unsaturation.

Found %: P 13.92; 14.27 $C_9H_{19}O_4P$. Calculated %: P 13.95

b) Action of sodium diethyl phosphite on 3-bromo-3-methyl-2-butanone. An ethereal solution of sodium diethyl phosphite was prepared from 4.9 g of sodium and 29.3 g of diethyl hydrogen phosphite. This

was added to an ethereal solution of 35 g of the bromo ketone. Heat was evolved, and the ether boiled. When reaction was complete, the mixture was heated in a water bath for one hour. Sodium bromide settled well. Fractionation of the colorless solution gave: Fraction I, b.p. 44-131° (28 mm), Fraction II, (13 g) b.p. 131-137° (17 mm), and Fraction III (15 g), b.p. 137-190° (10 mm).

By fractionation through a Widmer column, two substances were isolated.

The first (13 g) had b.p. 103-103.5° (5 mm); n_D^{20} 1.4360; d_0^{20} 1.0592; found MR 54.88; calculated MR 54.64. Titration with bromine gave about 2% unsaturation.

Found %: P 14.18 $C_9H_{19}O_4P$. Calculated %: P 13.95

The second substance (11 g) had b.p. 168 – 171° (4 mm); n_D^{20} 1.4445; d_0^{20} 1.1375; found MR 84.19; calculated MR 85.49

Found %: P 18.03; 17.75 $C_{13}H_{30}O_7P_2$. Calculated %: P 17.12

According to its analysis and high boiling point it corresponds most closely to the product of the addition of a second diethyl hydrogen phosphite molecule to diethyl 1,1-dimethylacetonylphosphonate:

$$CH_3 - CO - C(CH_3)_2 - P(O)(OC_2H_5)_2 + (C_2H_5O)_2POH \rightarrow$$

$$\rightarrow CH_3 - \underset{\displaystyle O=P-(OC_2H_5)_2}{\overset{\displaystyle OH}{C}} - C(CH_3)_2 - \overset{\displaystyle O}{\overset{\|}{P}}(OC_2H_5)_2$$

Its structure requires further elucidation.

c) Methylation of diethyl 1-methylacetonylphosphonate. By the addition of diethyl 1-methylacetonylphosphonate (prepared by methylation of acetonylphosphonic ester) to 3 g of potassium in 80 ml of dry dioxane with warming, a solution of the potassium derivative was prepared; the potassium derivative crystallized out when this solution was cooled. Methyl iodide (17 g; the theoretical amount is 11 g) was added, and potassium iodide was precipitated. The mixture was finally heated in a water bath for one hour. Potassium iodide and dioxane were removed, and distillation gave 9 g of product, b.p. 111-119° (12 mm). Distillation through a Widmer column gave a fraction of b.p. 114° (8 mm); n_D^{20} 1.4380; d_0^{20} 1.0645; found MR 54.81; calculated MR 54.64. Titration with bromine gave 0.4% unsaturation.

8. Synthesis of Diethyl 2-Oxobutylphosphonate by the Action of 1-Bromo--2-butanone on Triethyl Phosphite. Triethyl phosphite (28 g) was added dropwise to 1-bromo--2-butanone (26 g) heated to 120°; 16.5 g (theory requires 19 g) of ethyl bromide distilled off. Toward the end of the reaction the bath temperature was raised to 185°. Distillation gave: Fraction I, b.p. 64-101° (0.5 mm), and Fraction II (23.5 g), b.p. 100-101° (0.5 mm). Redistillation gave a fraction of b.p. 99-100° (0.5 mm) and 133-134.5° (10 mm); n_D^{20} 1.4360, d_0^{20} 1.0917; found MR 49.86; calculated MR 50.02. Titration with bromine gave 5% unsaturation.

Found %: P 14.53 $C_8H_{17}O_4P$. Calculated %: P 14.88

SUMMARY

1. The results reported point to an analogy between β-keto and β-alkoxycarbonyl derivatives of phosphonic and carboxylic esters.

2. Phosphonoacetic and 2-phosphonopropionic triesters do not contain appreciable amounts of the enol forms.

3. Titration with bromine indicates that acetonylphosphonic and 1-methylacetonylphosphonic esters contain small amounts of the enol forms. Considerable enolization occurs in an alkaline medium.

4. β-keto phosphonic esters prepared by the A. E. Arbuzov rearrangement differ in their properties from

sodium diethyl phosphite.

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OXIDATION-REDUCTION SYSTEMS FOR THE INITIATION OF FREE-RADICAL PROCESSES

COMMUNICATION 2. INITIATION OF POLYMERIZATION IN AQUEOUS EMULSIONS BY REVERSIBLE SYSTEMS AT TEMPERATURES BELOW 0°, AND A STUDY OF THE MICROSTRUCTURE OF THE POLYMER CHAIN

G. P. Belonovskaya, B. A. Dolgoplosk, and E. I. Tinyakova

In the preceding communication [1] we examined the mechanism of the action of an oxidation-reduction system consisting of a dienol, cumene hydroperoxide, and a very small amount of an iron or copper salt, and we showed that it can be effectively applied for the initiation of polymerization in aqueous emulsions at about 0°. The object of the present investigation was the application of this system in the initiation of polymerization in aqueous emulsions at lower temperatures with a view to studying the relation between polymerization temperature and the microstructure of the polymer chain.

It is known that the kinetics of polymerization in emulsions is to a considerable extent determined by the identity of the hydroperoxide. In a study of a system containing thiols and the iron pyrophosphate complex, Fryling and Follet [2], and also Orr and Williams [3], showed that replacement of cumene hydroperoxide by its alkyl derivatives considerably raises the activity of the system in the polymerization process. The authors associate the change in the polymerization kinetics mainly with the change in the distribution of the hydroperoxide between the aqueous and hydrocarbon phases. Similar results were obtained in work with systems containing polyamines and iron salts [4, 5, and others]. The authors find that the systems studied are most active in presence of p-tert-butylisopropylbenzene hydroperoxide. It was considered to be necessary to study the initiating activity of variants of our system in which different hydroperoxides are used.

EXPERIMENTAL

1. Initiation of Polymerization at 5°. The system used contained dihydroxymaleic acid, an iron salt, and a hydroperoxide, namely cumene, diisopropylbenzene, or p-tert-butylisopropylbenzene hydroperoxide. The dihydroxymaleic acid amounted to 0.3% on the amount of hydrocarbons, cumene hydroperoxide to 0.5% on the amount of hydrocarbons, and the amounts of the other hydroperoxides were equivalent to that of cumene hydroperoxide. The results of various experiments are given in Table 1.

The results show that the system containing dihydroxymaleic acid and an iron salt has maximum activity in presence of p-tert-butylisopropylbenzene hydroperoxide.

Similar results were obtained for the effect of the structure of the hydroperoxide on the activity of the system containing ascorbic acid and an iron salt (Table 2). The ascorbic acid amounted to 0.1% on the amount of hydrocarbons, cumene hydroperoxide to 0.2% on the amount of hydrocarbons, and the amounts of the other hydroperoxides were equivalent to that of cumene hydroperoxide.

The results showed that replacement of cumene hydroperoxide by the equivalent amount of p-tert-butylisopropyl hydroperoxide considerably raises the effectiveness of the system in polymerization. By taking advantage of this fact we were able to effect polymerization at very low temperatures.

TABLE 1

Effect of the Structure of the Hydroperoxide on the Copolymerization of Butadiene and Styrene

(70 : 30) at 5°; pH ≃ 3

Hydroperoxide	Isopropylbenzene	Diisopropylbenzene	p-tert-butylisopropylbenzene
Yield of polymer in 18 hrs. (%)	56-60	50-55	85-90

TABLE 2

Effect of the Structure of the Hydroperoxide on the Polymerization of Butadiene

−15°; pH ≃ 3

Hydroperoxide	Isopropylbenzene	Diisopropylbenzene	p-tert-butylisopropylbenzene	diisopropylbenzene dihydroperoxide
Yield of polymer in 9 hrs. (%)	32.5	36.0	43.0	13.7

2. Initiation of Polymerization at Low Temperatures (down to − 47°).

Polymerization at − 25, − 35, and − 47° was carried out in a special apparatus having a glycerol-sealed stirrer, cooling being applied with a mixture of acetone and solid carbon dioxide. In order to prevent the aqueous phase freezing, a suitable amount of glycerol was added to the water. The experiments were carried out with exclusion of air in a medium freed from oxygen with the aid of nitrogen.

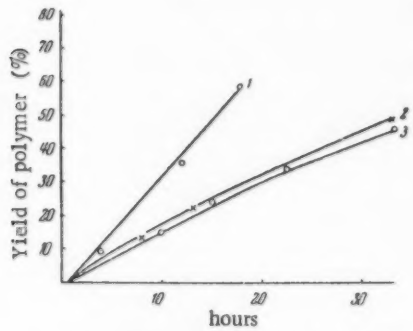


Fig. 1. Polymerization kinetics at − 25° in an acid medium (pH 3) with a system containing dihydroxymaleic acid: 1) 70 : 30 mixture of butadiene and styrene; 2) isoprene; 3) butadiene.

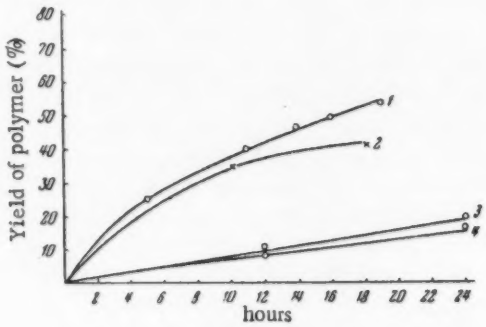
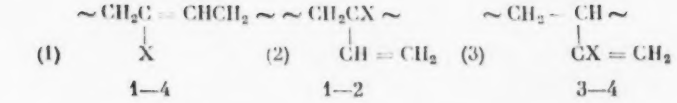


Fig. 2. Polymerization kinetics at − 35 and − 47° in an acid medium with a system containing ascorbic acid: 1) butadiene at − 35°; 2) isoprene at − 35°; 3) butadiene at − 47°; isoprene at − 47°.

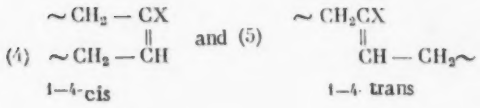
The system containing dihydroxymaleic acid and p-tert-butylisopropylbenzene hydroperoxide is effective for polymerization at − 25° in an acid medium when 6 mole % of Mohr's salt (based on the amount of hydroperoxide) is added (Fig. 1). At − 35 and − 47° the dihydroxymaleic system is ineffective for polymerization even when very large amounts of Mohr's salt are added (more than 15 mole % of the hydroperoxide). At these temperatures polymerization was effected in presence of ascorbic acid, p-tert-butylisopropylbenzene peroxide, and 0.8-1.6 mole % of Mohr's salt. At − 35 and − 47° we prepared butadiene-styrene copolymer, polybutadiene, and polyisoprene (Fig. 2).

3. Relation of the Structure of the Polymer Chain to the Polymerization Temperature. In the polymerization of dienes, the microstructure of the polymer chain is characterized by the following possible unit structures:

1-4, 1-2, and 3-4 structures



cis and trans structures



Available data on the structure of butadiene polymers [6-8 and others] show that in polymerization by the free-radical mechanism, change in temperature does not have any substantial effect on the relative amounts of 1-4 and 1-2 repeating units, but considerably affects the relative amounts of cis and trans 1-4 units. As the polymerization temperature falls, the number of trans units increases. It was considered desirable to study the structures of isoprene and butadiene polymers prepared over a wide range of polymerization temperatures with the aid of the oxidation-reduction system studied.

Butadiene and isoprene polymers prepared over a temperature range of about 100° (from + 50 to − 47°), purified by a double reprecipitation with methanol from a 2% benzene solution, and vacuum-dried at room temperature were investigated for the contents of 1-2 (3-4) and 1-4 monomer units.* The experimental results are given in Table 3.

TABLE 3

Contents of 1-2 (3-4) and 1-4 Monomer Units in Butadiene and Isoprene Polymers in their Relation to Polymerization Temperature

No.	Polymer	Polymerization temperature (°C)	Contents of monomer units			
			1-2	3-4	1-4	
					cis	trans
1	Polybutadiene	−35	17	—	0	83
2	"	−15	17	—	4	79
3	"	+5	18	—	10	72
4	Polyisoprene	−47	8.0	6.0	0	86
5	"	−35	8.0	5.0	0	87
6	"	−25	7.0	4.0	0	89
7	"	+50	7.0	5.0	8,0	80

The contents of 1-2 and 3-4 units in the polybutadiene and polyisoprene chains for the given range of polymerization temperatures remain almost constant. With rise in temperature the proportion of cis 1-4 units in the chains increases. For polybutadiene at a polymerization temperature of − 35°, all the 1-4 units are in the trans form; for polyisoprene the same effect is observed at somewhat higher temperatures. It was assumed earlier that the shift toward the trans form with lowering of polymerization temperature is due to change in the equilibrium between the cis and trans forms of the diene itself. However, Volkenshtein and others showed that no change occurs in the relative amounts of the isomeric forms over the range from + 75 to − 60° [9]. We

* The structures of the monomer units were determined from the infrared-absorption spectra by K. V. Nelson.

consider that the relative number of cis and trans units in the chain is to be related to the cis-trans isomerization of polymeric allyl radicals in a stage of chain growth:

$$\sim CH_2-C(=CH_2)-X \rightleftarrows \sim CH_2-C(=CH_2)-X$$

Lowering of polymerization temperature displaces the equilibrium toward the more stable trans form.

In the polymerization of isoprene, approximately equal numbers of 1-2 and 1-4 units are formed in the chain, which points to equal probability of reaction of the diene with free radicals in the 1- and 4-positions:

$$R^{\cdot} + CH_2^{1}=CH^{2}-C^{3}(CH_3)=CH_2^{4} \xrightarrow{I} R-CH_2^{1}-CH^{2}=CH_2^{1}-C^{3}(CH_3)=CH_2^{4}$$

$$R-CH_2^{4}-C^{3\cdot}(CH_3)-CH_2^{1}-CH^{2}=CH_2^{1}$$

Our experimental results enabled us, in conjunction with Poddubny and Nelson, to advance the hypothesis that 1-4 units, which mainly determine the structure of the whole chain, are probably disposed with equal probability in the head-to-tail and head-to-head positions, so that the polymer has an irregular structure. This irregularity is probably the explanation of the inability of polyisoprene to undergo orientation and crystallization, in spite of the fact that the chain consists entirely of trans units and contains very few 1-2 and 3-4 units. In the case of polybutadiene, in which this irregularity factor cannot occur, lowering of polymerization temperature with the resulting formation of pure trans isomer leads to the appearance of marked crystallization effects.

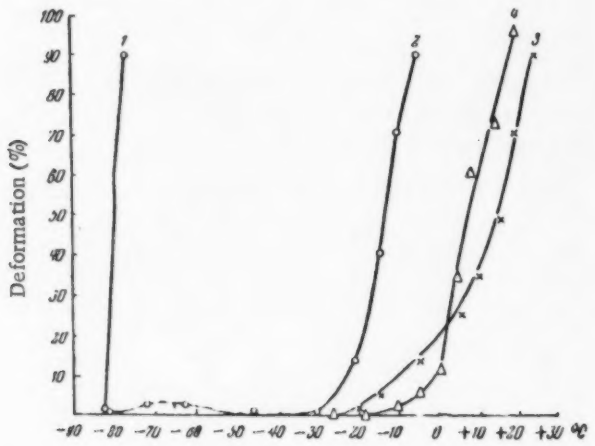
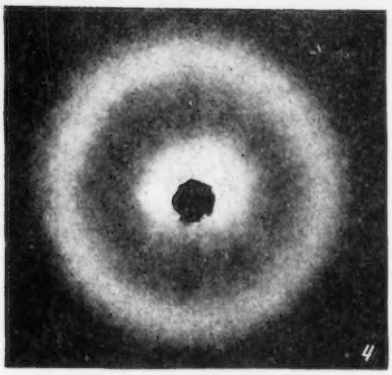
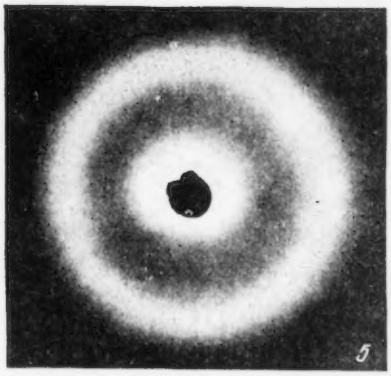
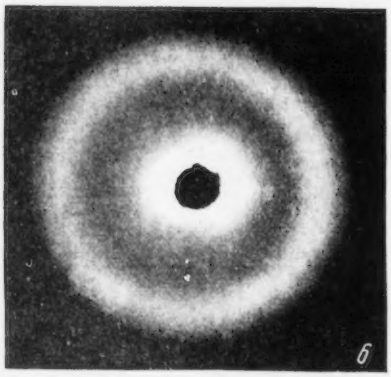


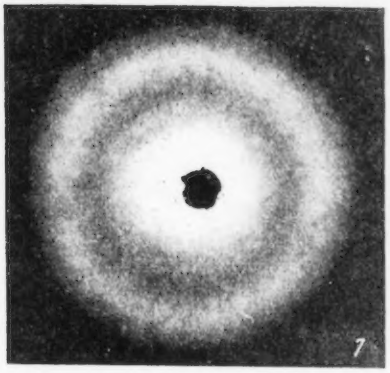
Fig. 3. Dependence of the deformation of butadiene polymer on polymerization temperature: 1) 60°; 2) 5°; 3) − 25°; 4) − 35°

x-Ray investigations on stretched samples of butadiene polymer showed that with lowering of the polymerization temperature the content of crystalline phase in the polymer increases [8, 10, 11, and others]. The crystallizability of polymers can be characterized also by the rate of deformation of a sample of the polymer under the action of a constant load with gradual rise of temperature starting from a temperature below the vitrification point. The crystallizability of butadiene polymers which we prepared at various temperatures were studied by a method recommended to us by A. I. Marei. It follows from Fig. 3, in which results are given









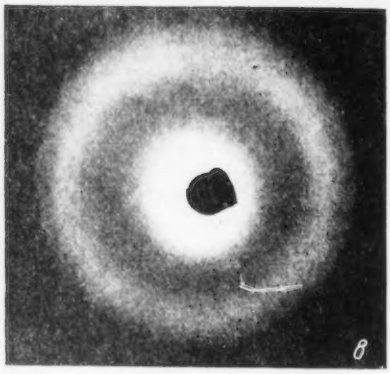


Fig. 4. x-Ray diffraction photograph of polybutadiene prepared at 5°
Fig. 5. x-Ray diffraction photograph of polybutadiene prepared at − 15°
Fig. 6. x-Ray diffraction photograph of polybutadiene prepared at − 25°
Fig. 7. x-Ray diffraction photograph of polybutadiene prepared at − 35°
Fig. 8. x-Ray diffraction photograph of polybutadiene prepared at − 47°

for butadiene polymers prepared at 60, 5, − 25, and − 35°, that the tendency to crystallize is determined by the polymerization temperature. This view was confirmed by x-ray investigations on polybutadiene rubbers. *

* The x-ray investigations were carried out by S. G. Strunsky.

The x-ray photographs (Figures 4-8) show that with lowering of polymerization temperature butadiene polymers show an increasing tendency to crystallize, and in polymers prepared at − 25, − 35, and − 47° there is an appreciable amount of crystalline phase, even in unstretched samples, at room temperature.

SUMMARY

1. It was shown that it is possible to use systems containing dienols, organic hydroperoxides, and iron salts for the initiation of polymerization at temperatures down to − 47°.

2. It was established experimentally that there is a relation between the polymerization temperatures of butadiene and isoprene and the microstructures of their polymer chains. The mechanism on which this relation is based is discussed.

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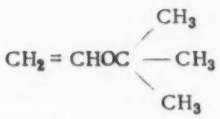
REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 7. COPOLYMERIZATION OF tert-BUTYL VINYL ETHER WITH METHYL METHACRYLATE

M. F. Shostakovsky, A. M. Khomutov, and V. I. Belyaev

In previous papers [1-3] we described the copolymerization of some vinyl ethers with methacrylic acid and its methyl ester. In these investigations a relation was established between the structures of the monomers and their behavior toward the initiators used to bring about polymerization. Particular account must be taken of this fact in the study of the free-radical mechanism of the polymerization of vinyl ethers [4-6], which has not yet been adequately explored. In the present paper we describe the regularities observed in the copolymerization of tert-butyl vinyl ether with methyl methacrylate. Vinyl ethers of primary and secondary alcohols are compounds of high reactivity with a marked tendency to undergo ion-induced transformations [7]. In tert-butyl vinyl ether

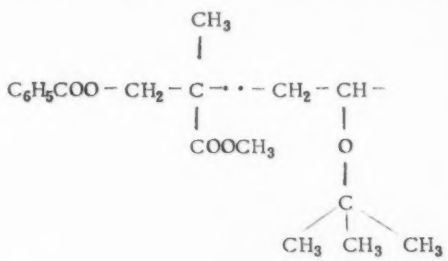


(I)

this property is enhanced – the compound hydrolyzes even in absence of acids. Its high activity is shown also in reactions such as the addition of alcohols and phenols. This ether readily polymerizes by the ionic mechanism. The occurrence of polymerization by the free-radical mechanism has not been established for tert-butyl vinyl ether with benzoyl peroxide or 2,2' - azobis [2-methylpropionitrile] as initiator. This behavior is different from that of other vinyl ethers. The reduced tendency of tert-butyl vinyl ether to undergo polymerization by the free-radical mechanism is, of course, associated with its structure.

In the present investigation we prepared copolymers of tert-butyl vinyl ether and methyl methacrylate, and it was found that the yield depends on the chemical structure of the initiator. For example, the yields of copolymers obtained in presence of benzoyl peroxide were considerably lower than those obtained in presence of the azo nitrile. When a comparison is made between the yields of copolymers of tert-butyl vinyl ether with methyl methacrylate with those of copolymers of n-butyl vinyl ether with methyl methacrylate, it will be noted that the latter are formed in higher yield (Table 1).

The lower yields of copolymers of methyl methacrylate with tert-butyl vinyl ether are to be explained by the low activity of a polymerization chain having a terminal tert-butyl vinyl ether unit with a free valency:



(II)

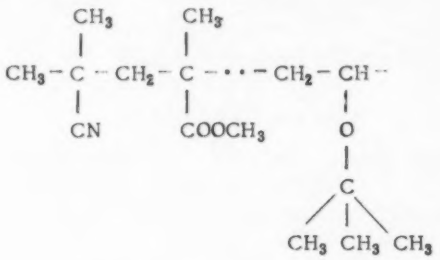
TABLE 1

Comparison of the Compositions of the Copolymers of n-Butyl Vinyl Ether and of tert-Butyl Vinyl Ether with Methyl Methacrylate

Initiator and composition of copolymer	Yield (%)	Monomer units in copolymer	
		Methyl methacrylate (%)	Alkyl vinyl ether (%)
Benzoyl peroxide			
Copolymer of methyl methacrylate with n-butyl vinyl ether in a molar ratio of 1:3	32.26	74.0	26.0
Copolymer of methyl methacrylate with tert-butyl vinyl ether in a molar ratio of 1:3	2.05	72.3	27.6
2,2'-Azobis[2-methylpropionitrile]			
Copolymer of methyl methacrylate with n-butyl vinyl ether in a molar ratio of 1:3	30.48	63.75	36.25
Copolymer of methyl methacrylate with tert-butyl vinyl ether in a molar ratio of 1:3	21.20	78.33	21.67

This radical has a low tendency to combine with either of the monomers.

The use of the azo nitrile leads to the formation of a polymerization chain of the following structure:

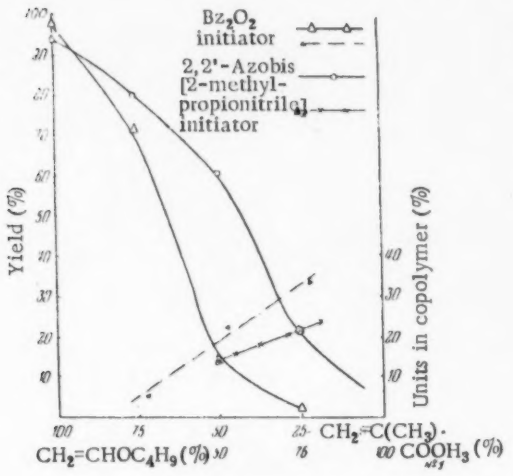


(III)

As experiment shows, such a chain has a higher activity. Hence, in these reactions the character of the initiator and the structure of the complex radicals are of great importance. The parts played by these factors have been demonstrated for other cases in previous investigations [2]. A comparative study of the properties of copolymers of methyl methacrylate with various vinyl ethers (tert-butyl vinyl ether and vinyl ethers of primary and secondary alcohols) shows that there are some regular features common to these copolymerizations. In all cases, with increase in the vinyl ether content of the reaction mixture, yields are reduced and the proportion of vinyl ether units in the copolymer chain is increased. This is illustrated in the figure.

These regularities are general, both for benzoyl peroxide and for the azo nitrile as initiator. There are some peculiar features, however. For example, when methyl methacrylate is in excess in the reaction phase, the azo nitrile does not bring about copolymerization: methyl methacrylate polymer is formed. Formation of copolymers is observed only for equimolecular amounts of the monomers and for excess of tert-butyl vinyl ether. For example, in the copolymerization of 5 mole % of methyl methacrylate and 95 mole % of

tert-butyl vinyl ether, a mixture of copolymers containing 40, 17, and 18.8% of tert-butyl vinyl ether units was obtained.



EXPERIMENTAL

The following freshly distilled substances were used: methyl methacrylate of b.p. 100.5°, n_D^{20} 1.4150, and d_4^{20} 0.9361, and tert-butyl vinyl ether of b.p. 75-76°, n_D^{20} 1.4003, and d_4^{20} 0.7691.

The copolymerizations were carried out in sealed glass tubes at 60 ± 1°. The initiators used were benzoyl peroxide and 2,2' -azobis [2-methylpropionitrile]. The reaction components were taken in various molar proportions. Reaction proceeded continuously until solid or viscous products were obtained (96 hours). The tubes were then cooled to 0°. The reaction products were dissolved, reprecipitated, and then extracted until reaction for a double bond was absent. The resulting copolymers were treated with selective solvents and dried in a vacuum to constant weight. The polymers and copolymers were analyzed for carbon and hydrogen, and their compositions were calculated.

In order to verify the ability of the monomers to undergo free-radical polymerization under these conditions, control-polymerization experiments were carried out.

1. Copolymerization of Methyl Methacrylate with tert-Butyl Vinyl Ether in Presence of Benzoyl Peroxide. Reaction was between 2.5 g (0.025 mole) of methyl methacrylate and 2.5 g (0.025 mole) of tert-butyl vinyl ether. The reaction conditions are described above. The liquid reaction product was vacuum-fractionated at 25-27°. Liquid of n_D^{20} 1.4098 (1.8 g) was collected, and this was found, by the bisulfite method, to contain 0.54 g of unchanged vinyl ether; the remainder, 1.26 g, was taken to be methyl methacrylate. The residue in the distilling flask was a highly viscous liquid; it was dissolved in benzene by the application of heat and precipitated with methanol. In this way 0.757 g of copolymer was isolated. In the liquid remaining after separation and purification of the copolymer, 0.27 g of methyl methacrylate and 1.08 g of tert-butyl vinyl ether were found.

The copolymer isolated was investigated for solubility by tests with a series of solvents. It was found that the copolymer was soluble in 1 : 1 ethanol-ether, whereas polymethyl methacrylate is insoluble in this mixture. The copolymer was dried to constant weight (within 0.0001 g) and analyzed for carbon and hydrogen.

The copolymerization of methyl methacrylate with tert-butyl vinyl ether was investigated by the above-described method for other monomer ratios. The relative amounts of monomers taken, the yields, and the compositions of the copolymers are given in Table 2.

When heated with benzoyl peroxide, tert-butyl vinyl ether did not form a polymer, but remained unchanged (n_D^{20} 1.4002).

2. Copolymerization of Methyl Methacrylate with tert-Butyl Vinyl Ether in Presence of 2,2' -Azobis [2-methylpropionitrile]. Reaction was between 2.5 g (0.025 mole) of methyl methacrylate and 2.5 g (0.025 mole) of tert-butyl vinyl ether. The reaction conditions are described above. The contents of the tube, which were very viscous, were dissolved in benzene and precipitated with methanol. The copolymer was dried to constant weight and analyzed for carbon and hydrogen. The solution remaining after the precipitation and purification of copolymer was found by titration to contain 0.144 g of methyl methacrylate and 1.545 g of tert-butyl vinyl ether. The copolymerization of the same monomers at other molar ratios was investigated in a similar way. The results of the investigations are given in Table 3.

It must be mentioned that the copolymers obtained at molar ratios of methyl methacrylate and tert-butyl

TABLE 2

Yields and Compositions of Copolymers of Methyl Methacrylate (I) with tert-Butyl Vinyl Ether (II) (Initiator – benzoyl peroxide)

Molecular proportions of monomers taken (%)		Yield (%)	Elementary composition		Monomer units in copolymer (%)	
(I)	(II)		C (%)	H (%)	(I)	(II)
100	—	97.2	59.98 59.98	8.16 8.21	100	—
75	25	71.48	60.59 60.62	8.63 8.70	97	3
50	50	13.80	62.56 62.31	8.90 8.66	79.66	20.34
25	75	2.05	63.05 63.60	8.61 8.72	72.3	27.7
—	100		No polymerization		—	—

vinyl ether of 1 : 3 and 1 : 19 were precipitated by hexane owing to their partial solubility in methanol and complete solubility in ethanol and ether. A copolymer was isolated also which was insoluble in methanol and gave duplicate carbon contents of 61.92% and 62.31%, which corresponds to a copolymer containing 81.2% methyl methacrylate units and 18.8% tert-butyl vinyl ether units.

TABLE 3

Yields and Compositions of Copolymers of Methyl Methacrylate (I) with tert-Butyl Vinyl Ether (II)

(Initiator – 2,2' -azobis [2-methylpropionitrile])

Molecular proportions of monomers taken %		Yield (%)	Elementary composition		Monomer units in copolymer (%)	
(I)	(II)		C (%)	H (%)	(I)	(II)
100	—	94.5	59.98 59.98	8.16 8.21	100	—
95	5	90.6	59.65 59.65	7.99 8.05	100	—
75	25	81.6	59.98 59.98	8.16 8.21	100	—
50	50	60.6	61.45 61.59	8.87 8.72	87.33	12.67
25	75	21.2	62.65 62.55	9.27 9.36	78.33	21.67
5	95	8.2	64.92 64.72	9.67 9.79	59.83	40.17
—	100		No polymerization			

When heated with the azo nitrile, tert-butyl vinyl ether did not form a polymer, but remained unchanged.

SUMMARY

1. The copolymerization reaction of methyl methacrylate with tert-butyl vinyl ether was investigated, and some of their copolymers were prepared.

2. It was established that the content of tert-butyl vinyl ether residues in the copolymer with methyl methacrylate increases with increase in the concentration of the vinyl ether in the original monomer mix.

3. tert-Butyl vinyl ether does not polymerize in presence of benzoyl peroxide or of 2,2' -azobis [2-methylpropionitrile].

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 8. VINYL ETHERS OF 2-DIMETHYLAMINOETHANOL AND 2-(2,5-DICHLOROANILINO) ETHANOL

M. F. Shostakovsky and I. A. Chekulaeva

A systematic study of the properties of various vinyl ethers of ethanolamines enabled us to reveal and explain the relationship that exists between the character of the amino group and the reactivity of the vinyl ether [1-6]. Vinyl ethers containing a primary or secondary amino group are inert in ion-induced reactions [1, 2]. Replacement of the hydrogens of the amino group by alkyl and, particularly, phenyl radicals results in increased reactivity in the vinyl ether [3-5]. This relationship was found to hold also for the vinyl ethers of 2-dimethylaminoethanol $CH_2 = CHOCH_2CH_2N(CH_3)_2$ (I) and of 2-(2,5-dichloroanilino) ethanol $CH_2 = CHOCH_2CH_2NHC_6H_3Cl_2$ (II), which were found to be similar in properties to vinyl ethers of ethanolamines containing amino groups of similar character. Thus, the vinyl ether of 2-dimethylaminoethanol (I) has almost the same properties as the vinyl ether of 2-diethylaminoethanol $CH_2 = CHOCH_2CH_2N(C_2H_5)_2$ [3]. With alcohols it gives acetals:

$$CH_2 = CHOCH_2CH_2N(CH_3)_2 + HOCH_2CH_2N(CH_3)_2 \rightarrow$$

$$\rightarrow CH_3CH[OCH_2CH_2N(CH_3)_2]_2. \qquad \text{(III)}$$

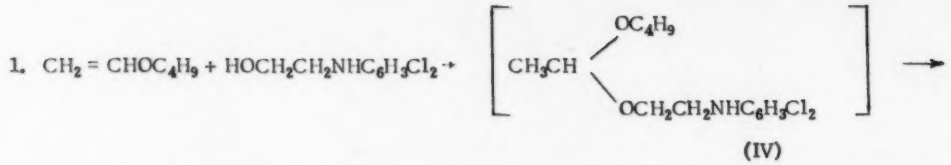
Reaction requires long heating at 100°, and the yield of the acetal (III) is only 4-5%. The vinyl ether (I) also does not polymerize in presence of ionic catalysts (ferric chloride, concentrated hydrochloric acid).

The vinyl ether of 2-(2,5-dichloroanilino) ethanol (II) is similar to the vinyl ether of 2-anilinoethanol $CH_2 = CHOCH_2CH_2NHC_6H_5$ [4]. Owing to the high mobility of the nitrogen-attached hydrogen, it readily undergoes the following changes in presence of traces of concentrated hydrochloric acid:

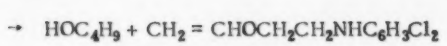
$$CH_2 = CHOCH_2CH_2NHC_6H_3Cl_2 + CH_2 = CHOCH_2CH_2NHC_6H_3Cl_2 \rightarrow$$

$$\rightarrow \left[CH_3CH \begin{array}{l} \diagup OCH_2CH_2NHC_6H_3Cl_2 \\ \diagdown NCH_2CH_2OCH = CH_2 \\ \qquad\quad | \\ \qquad\quad C_6H_3Cl_2 \end{array} \right] \rightarrow HOCH_2CH_2NHC_6H_3Cl_2 + (C_{12}H_{13}ONCl_2)_2$$

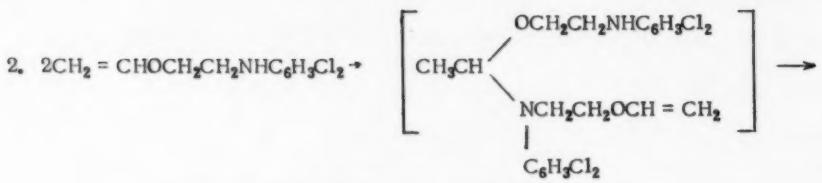
Owing to the readiness with which this reaction occurred, it was not found possible to effect addition of alcohols and ion-induced polymerization. No cyclic acetal of the oxazolidine type is formed, probably owing to steric hindrance. It was noted also that no cyclic acetal was present in the products of the reaction of butyl vinyl ether with 2-(2,5-dichloroanilino) ethanol, a fact that distinguishes this amino alcohol from 2-anilinoethanol [4]. We isolated only the substances (V) — (VIII), formed probably in the following way:



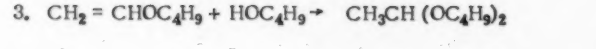
(IV)



(V)

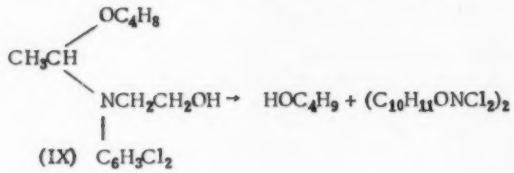


(VI) (VII)



(VIII).

The required acetal (IV) was found to be unstable: it decomposed when vacuum-distilled (3-5 mm). It is possible that, apart from the above compounds, the acetal (IX) is formed and is decomposed as follows:



(IX)

The vinyl ethers (I) and (II) were prepared by the vinylation of the corresponding amino alcohols; for the ether (II) reaction proceeded in presence of potassium hydroxide as catalyst, but for the ether (I) the alkoxide was required.

EXPERIMENTAL *

Vinyl Ether of 2-Dimethylaminoethanol (I). 2-Dimethylaminoethanol was prepared from ethylene oxide and 33% aqueous dimethylamine; the amino alcohol was isolated from aqueous solution by repeated distillation with benzene. The potassium alkoxide was prepared by reaction of 2-dimethylaminoethanol with potassium (added gradually in small pieces at 15-20°). A mixture of 68 g of 2-dimethylaminoethanol (b.p. 135-136° and n_D^{20} 1.4300), 7.3 g of the potassium alkoxide, and 150 ml of benzene was prepared in a 2-liter rotating autoclave, and acetylene was passed in to a pressure of 14-16 atm. The autoclave was heated to 140-150° and maintained at that temperature for 5-6 hours. In the course of this time the amount of acetylene required for vinylation was absorbed. The reaction product was distilled, at first at reduced pressure, and then at atmospheric pressure. When the benzene had come over, the following fractions were obtained:

Fraction I, b.p. 95 – 110°; 41.4 g
Fraction II, b.p. 110 – 120°; 20.3 g
Fraction III, b.p. 120 – 124°; 25.6 g (29.3%)
Resin, 17.9 g

* Laboratory worker V. A. Zabavina and student T. T. Minakova took part in the experimental work.

Fraction III was treated with sodium, and distillation then gave 24 g of the vinyl ether of 2-dimethylaminoethanol, a colorless liquid with an amine odor; b.p. 123 – 124°; n_D^{20} 1.4242; d_4^{20} 0.8377; found MR 35.1; M (cryoscopically in benzene) 110.7; 112.2; calculated for $C_6H_{13}ON$ MR 35.02; M 115.1

	Found %:	C 62.21;	62.38;	H 11.29;	11.25;	N 12.00;	11.81
$C_6H_{13}ON$.	Calculated %:	C 62.61;		H 11.38;		N 12.16	

The vinyl ether was readily hydrolyzed with 2% sulfuric acid at room temperature with formation of acetaldehyde and the amino alcohol; found for content of vinyl ether: 98.4; 98.7%. The literature gives b.p. 50° (16 mm) [7]; b.p. 124° (760 mm); n_D^{20} 1.4235 [8].

Fractions I and II consisted of the required vinyl ether containing some benzene, which could be removed only by distillation through a column.

The addition of alcohols to the vinyl ether of 2-dimethylaminoethanol was carried out in a three-necked flask fitted with stirrer and thermometer. A mixture of 8.9 g (0.077 mole) of the vinyl ether of 2-dimethylaminoethanol and 6.9 g (0.07 mole) of 2-dimethylaminoethanol (b.p. 135 – 136°; n_D^{20} 1.4300) was heated to 95-100°, 2-3 drops of concentrated hydrochloric acid were added, and the temperature was maintained at 95-100° for 15-18 hours. Vacuum distillation of the reaction products gave:

Fraction I, b.p. 26 – 35° (10 mm); n_D^{20} 1.4267; 13.8 g
Fraction II, b.p. 100 – 103° (10 mm); n_D^{20} 1.4347; 0.7 g (4.5%)
Resin, 1.3 g

Fraction I was a mixture of starting materials. Fraction II was purified by redistillation under reduced pressure, and the required acetal was isolated as a colorless mobile liquid, b.p. 98.5 – 99° (8 mm), n_D^{20} 1.4343; d_4^{20} 0.8952; found MR 59.46; calculated for $C_{10}H_{24}O_2N_2$ MR 59.54.

	Found %:	C 58.20;	58.23;	H 11.63;	11.62;	N 14.04;	13.93
$C_{10}H_{24}O_2N_2$.	Calculated %:	C 58.79;		H 11.84;		N 13.71	

Vinyl Ether of 2-(2,5-Dichloroanilino) ethanol (II). The vinyl ether was prepared from 2-(2,5-dichloroanilino) ethanol * by the method described above for (I), with the exception that potassium hydroxide was used as catalyst and the reaction temperature was maintained at 190-200°. The reaction product was isolated by vacuum distillation, and 14.0 g of 2-(2,5-dichloroanilino) ethanol (m.p. 49-51°) gave:

Fraction I, b.p. 125 – 150° (8 mm); n_D^{19} 1.5830; 1.4 g
Fraction II, b.p. 150 – 151° (7.5 mm); n_D^{19} 1.5728; 8.3 g
Resin, 5.4 g

Refractionation of Fraction II under reduced pressure gave the vinyl ether of 2-(2,5-dichloroanilino) ethanol in the form of a light yellow viscous liquid, b.p. 135 – 137° (4 mm); 142 – 144° (5.5 mm); n_D^{20} 1.5725; d_4^{20} 1.2506; found MR 61.14; calculated for $C_{10}H_{11}ONCl_2$ MR 59.29. The difference between the determined and calculated values of the molecular refraction can, of course, be explained by the presence of a phenyl radical in the vinyl ether molecule.

	Found %:	C 51.84;	51.97;	H 4.89;	4.77;	N 5.87;	5.87; Cl 30.45; 30.11
$C_{10}H_{11}ONCl_2$.	Calculated %:	C 51.74;		H 4.77;		N 6.03;	Cl 30.59

As a result of the hydrolysis of the vinyl ether with 2% sulfuric acid at room temperature, we isolated 2-(2,5-dichloroanilino) ethanol, m.p. 49-50°, and acetaldehyde, which was determined by the bisulfite method.

Results of the vinylation of 2-(2,5-dichloroanilino) ethanol under other conditions are given in the table.

The investigation of the behavior of the vinyl ether of 2-(2,5-dichloroanilino) ethanol in presence of a catalytic amount of concentrated hydrochloric acid was carried out in a round-bottomed flask fitted with stirrer.

* We are indebted to K. D. Petrov for placing a supply of the amino alcohol at out disposal.

To 39.2 g of the ether at 20°, 2-3 drops of concentrated hydrochloric acid were added. In the course of 30 minutes the temperature rose to 35°: the reaction mixture thickened greatly and assumed a dark bordeaux color. Distillation of 38.3 g of reaction products gave:

Fraction I, b.p. 142 – 145° (5 mm); n_D^{20} 1.5728; 19.9 g
Fraction II, b.p. 146 – 190° (5 mm); 11.2 g
Thick resinous residue, 7.2 g

Fraction I was the original vinyl ether. Fraction II solidifed; it was washed with petroleum ether (b.p. 64-69°) and dried; it then consisted of 2-(2,5-dichloroanilino) ethanol, m.p. 49-51°. The resinous residue was dissolved in acetone, precipitated from solution with isopentane (b.p. 26-27°), and vacuum-dried (3-4 mm). This residue corresponded in analysis to $(C_{12}H_{13}ONCl_2)_2$. Found M (cryoscopically in benzene) 507; 520; calculated for $(C_{12}H_{13}ONCl_2)_2$ M 516.2.

	Found %:	C 55.87; 55.59	55.84;	H 5.10;	5.07;	Cl 28.43;	28.21;	N 5.71;
$C_{12}H_{13}ONCl_2$.	Calculated %:	C 55.81;		H 5.07;		Cl 27.50;		N 5.23

Experiment	Catalyst	Solvent	Reaction temperature (°C)	Duration of reaction (hours)	Yield of pure vinyl ether (%)
1	KOH	Benzene	190–200	5–6	52.54
2	"	Dioxane	190–200	5	41.5
3	"	"	150–160	5	55.0
4	"	"	70–80	5	—

Reaction of 2-(2,5-Dichloroanilino) ethanol with Butyl Vinyl Ether.

Concentrated hydrochloric acid (2 drops) was added to a stirred mixture of 26.8 g (0.13 mole) of 2-(2,5-dichloroanilino) ethanol (m.p. 49-50°) and 13.0 g (0.13 mole) of butyl vinyl ether (b.p. 92-93° and n_D^{20} 1.4028; it did not dissolve the amino alcohol) at 20°. The temperature rose rapidly to 65°, and a thick homogeneous dark-bordeaux reaction mixture was formed. The mixture was stirred for 4.5 hours and then set aside for 20 hours. Vacuum distillation of the reaction products gave 6.5 g of butyl alcohol (b.p. 115° and n_D^{22} 1.3988), 1.6 g of the dibutyl acetal (b.p. 184-185° and n_D^{21} 1.4083), 17.6 g of 2-(2,5-dichloroanilino) ethanol, and 13.6 g of solid residue. The residue was purified by a double reprecipitation with isopentane from acetone solution and was obtained as a sticky, viscous, red-brown product, which analysis indicated to be a mixture of $(C_{10}H_{11}ONCl_2)_2$ and $(C_{12}H_{13}ONCl_2)_2$. Found M (cryoscopically in benzene) 516; 497; calculated for $(C_{12}H_{13}ONCl_2)_2$ M 516.2; for $(C_{10}H_{11}ONCl_2)_2$ M 461.1

	Found %:	C 53.43; 5.68	53.23;	H 5.09;	5.02;	Cl 28.47;	27.94;	N 5.69;
$C_{12}H_{13}ONCl_2$.	Calculated %:	C 55.81;		H 5.07;		Cl 27.5;		N 5.23
$C_{10}H_{11}ONCl_2$.	Calculated %:	C 51.74;		H 4.77;		Cl 30.59;		N 6.03

SUMMARY

1. The vinyl ethers of 2-dimethylaminoethanol and of 2-(2,5-dichloroanilino) ethanol were prepared, and some reactions of these ethers were investigated.

2. The reaction of 2-(2,5-dichloroanilino) ethanol with butyl vinyl ether was studied.

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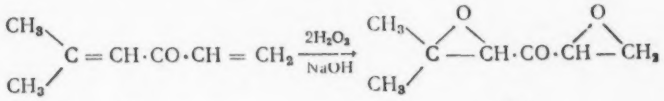
α-KETO EPOXIDES

COMMUNICATION 8. REACTIONS OF 1,2,4,5-DIEPOXY-5-METHYL-3-HEXANONE

I. N. Nazarov, A. A. Akhrem, and V. V. Kokhomskaya

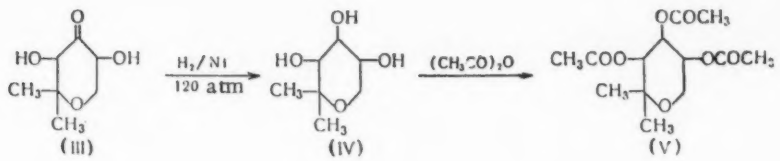
In a previous investigation [1] it was shown that, by the oxidation of 5-methyl-1,4-hexadien-3-one [2] with alkaline hydrogen peroxide in dioxane, the keto diepoxide (II) is formed in high yield:



(I) (II)

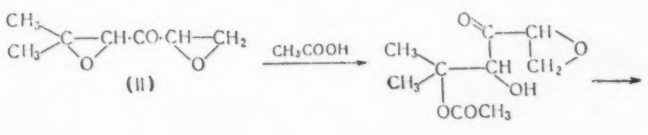
It was of interest to study the reactions of this readily accessible compound, which, as a result of the presence of two epoxy rings conjugated with a carbonyl group, is varied in its reactivity. The present communication is devoted to a study of the reactions of the α-keto diepoxide (II) with alcohols, acetic acid, amines, and other compounds containing mobile hydrogen. As we have shown previously [1], hydrolysis of the α-keto diepoxide (II) with water at room temperature gives tetrahydro-3,5-dihydroxy-2,2-dimethylpyran-4-one (III) in two stereoisomeric forms – a crystalline solid and a liquid.

Hydrogenation of tetrahydro-3,5-dihydroxy-2,2-dimethylpyran-4-one (III) (mixture of isomers) with hydrogen at 120 atm in presence of Raney nickel gave a high yield of tetrahydro-2,2-dimethylpyran-3,4,5-triol (IV), which was readily acetylated to the triacetic ester (V) with acetic anhydride:

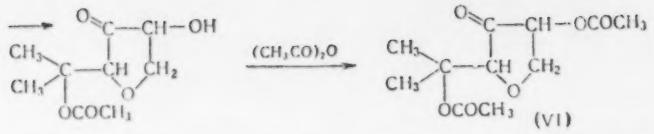


(III) (IV) (V)

Attempts to split the tetrahydropyrantriol (IV) with gaseous hydrogen chloride or concentrated hydrochloric acid, and also its triacetic ester (V) with acetyl chloride in presence of anhydrous zinc chloride, with the object of preparing polyhydroxy compounds were not successful. In all cases some of the original material was recovered unchanged and resinification occurred. When the α-keto diepoxide (II) was treated with glacial acetic acid and acetic anhydride at 150°, a diacetic ester was formed, which probably had a furan structure (VI):

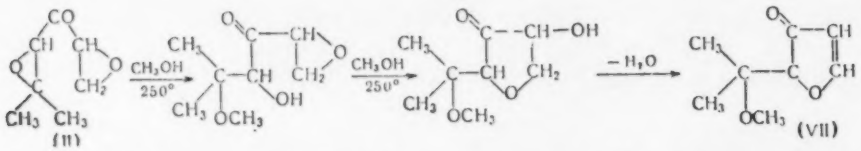


(II)



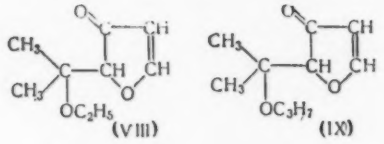
(VI)

Heating of the α-keto diepoxide (II) with methanol at 250° resulted in the isolation of a crystalline product which corresponded in composition to 2-(1-methoxy-1-methylethyl)-3(2H)-furanone (VII):



(II) (VII)

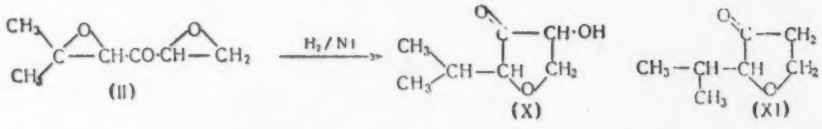
Addition of ethyl and isopropyl alcohols to the α-keto epoxide (II) went in a similar way with formation of 2-(1-ethoxy-1-methylethyl)-3(2H)-furanone (VIII) and 2-(1-isopropoxy-1-methylethyl)-3(2H)-furanone (IX), respectively:



(VIII) (IX)

The yield falls as the molecular weight of the alcohol increases.

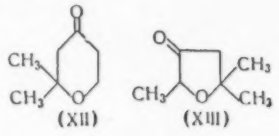
Hydrogenation of the α-keto diepoxide (II) at room temperature in presence of Raney nickel resulted in the formation of a mixture, from which we succeeded in isolating dihydro-4-hydroxy-2-isopropyl-3(2H)-furanone (X) and dihydro-2-isopropyl-3(2H)-furanone (XI):



(II) (X) (XI)

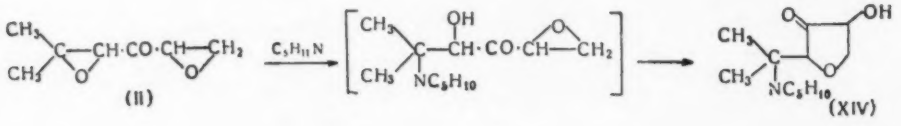
In this reaction a mixture of (X) and (XI) is formed both when two molecular proportions of hydrogen are absorbed and also when one molecular proportion is absorbed.

The known tetrahydro-2,2-dimethylpyran-4-one (XII) [2] and dihydro-2,5,5-trimethyl-3(2H)-furanone (XIII) [3] were not detected among the hydrogenation products.



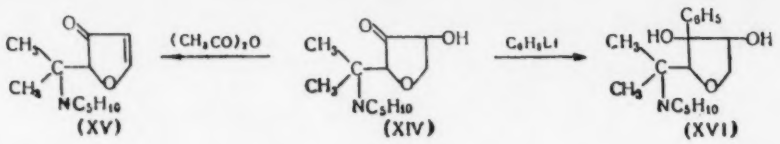
(XII) (XIII)

Reaction of the α-keto diepoxide (II) with 50% aqueous piperidine gave a high yield of dihydro-4-hydroxy--2-(1-methyl-1-piperidinoethyl)-3(2H-furanone (XIV):



(II) (XIV)

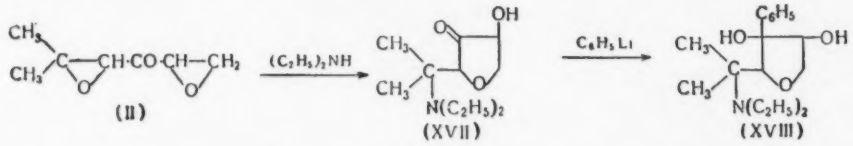
Under the action of acetic anhydride (XIV) is readily dehydrated with formation of 2-(1-methyl-1-piperidinoethyl)-3(2H)-furanone (XV), and by reaction with phenyllithium it gives tetrahydro-2-(1-methyl-1-piperidinoethyl)-3-phenyl-3,4-furandiol (XVI):



(XV) (XIV) (XVI)

Under the action of hydrogen chloride or picric acid, (XIV) and its dehydration product (XV) are readily deaminated with formation of piperidine hydrochloride or picrate, as previously observed in the case of the decomposition of aliphatic β-amino ketones [4]. With methyl iodide, (XIV) and its dehydration product (XV) give the corresponding methiodides. When the tetrahydrofurandiol (XVI) was treated with propionyl chloride, deamination again occurred with formation of piperidine hydrochloride, but we did not succeed in isolating the corresponding propionic esters. The synthesis of such esters interested us in connection with the search for new anesthetics.

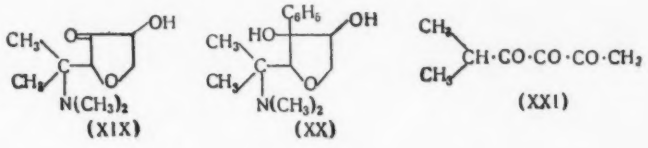
Reaction of the α-keto diepoxide (II) with aqueous diethylamine gave 2-(1-diethylamino-1-methylethyl) dihydro-4-hydroxy-3(2H)-furanone (XVII), which reacted with phenyllithium and gave 2-(1-diethylamino-1-methylethyl) tetrahydro-3-phenyl-3,4-furandiol (XVIII):



(II) (XVII) (XVIII)

When treated with hydrogen chloride, the amino hydroxy furanone (XVII) was deaminated with formation of diethylamine hydrochloride. We did not succeed in isolating a crystalline methiodide of (XVII).

Reaction of the α-keto diepoxide (II) with an aqueous solution of dimethylamine gave 2-(1-dimethylamino-1-methylethyl) dihydro-4-hydroxy-3(2H)-furanone (XIX), which reacted with phenyllithium and gave 2-(1-dimethylamino-1-methylethyl)tetrahydro-3-phenyl-3,4-furandiol (XX):



(XIX) (XX) (XXI)

The results of attempts to isomerize the α-keto diepoxide (II) into the tricarbonyl compound (XXI) in presence of boron trifluoride, anhydrous aluminum chloride, or concentrated sulfuric acid were obscure. In the case of anhydrous zinc chloride, two products were obtained – a liquid and a crystalline solid – of which the latter contained zinc. We have not yet been able to establish the structures of these products. The liquid product may be insufficiently purified 5-methyl-2,3,4-hexanetrione (XXI).

Treatment of the keto diepoxide (II) with sodiomalonic ester at − 5° gave a product, the structure of which we were unable to establish. We did not succeed in isolating it in the pure state, for it decomposed without distilling at a bath temperature of 203° and a residual pressure of 0.01 mm.

EXPERIMENTAL

Hydrogenation of the Tetrahydrodihydroxypyranone (III)

a) The solid isomer of the tetrahydrodihydroxypyranone (III) (11 g; m.p. 107-108°) [1] was dissolved in

100 ml of distilled water and hydrogenated at 98-110° in a rotating autoclave in presence of 2 g of Raney nickel and of hydrogen at a pressure of 120 atm. In the course of 4 hours 30 minutes 1.7 liters of hydrogen was absorbed, as compared with the calculated amount of 1.54 liters. The catalyst was separated, and vacuum fractionation of the product gave 9.5 g of tetrahydro-2,2-dimethylpyran-3,4,5-triol (IV) in the form of a colorless, highly viscous sirup, b.p. 150-151° (2 mm) and n_D^{20} 1.4910.

Found %: C 51.77; 51.68; H 8.59; 8.65
$C_7H_{14}O_4$. Calculated %: C 51.84; H 8.70

b) The liquid isomer of (III) (16.2 g; b.p. 107-109°/0.1 mm) [1] was dissolved in 150 ml of distilled water and hydrogenated as in the preceding experiment. The product, amounting to 8.3 g was the tetrahydropyrantriol (IV), a colorless, highly viscous sirup of b.p. 148.5-149° (1.5 mm) and n_D^{20} 1.4942.

Found %: C 51.80; 51.68; H 8.38; 8.51
$C_7H_{14}O_4$. Calculated %: C 51.84; H 8.70

c) By hydrogenation of a mixture of isomers of the tetrahydrodihydroxypyranone (II) under the same conditions, the tetrahydropyrantriol (IV) was obtained as a colorless, highly viscous sirup of b.p. 148-149° (1.5 mm) and n_D^{20} 1.4892.

Found %: C 51.39; 51.45; H 8.95; 9.07
$C_7H_{14}O_4$. Calculated %: C 51.84; H 8.70

Found %: OH 31.11; 33.08 (in pyridine)
$C_7H_{11}(OH)_3$. Calculated %: OH 31.46

Tetrahydro-2,2-dimethylpyran-3,4,5-triol Triacetic Ester (V)

A mixture of 10 g of the tetrahydropyrantriol (IV), 100 g of acetic anhydride, and 10 g of sodium acetate was heated in a boiling water bath for three hours. The reaction product was then poured into ice water (400 ml), neutralized with sodium bicarbonate, and extracted with ether; the extract was dried with anhydrous magnesium sulfate. Vacuum fractionation gave 15 g of the triacetic ester of tetrahydro-2,2-dimethylpyran-3,4,5-triol (V) as a colorless viscous sirup, b. p. 142 – 143° (2 mm); n_D^{20} 1.4452; d_4^{20} 1.1521; found MR 66.63; calculated MR 66.64.

Found %: C 54.10; 54.20; H 6.94; 7.04
$C_{13}H_{20}O_7$. Calculated %: C 54.16; H 6.99

Found: M 285.8; 285.2 (in benzene)
$C_{13}H_{20}O_7$. Calculated: M 288

Found %: CH_3CO 45.18; 45.78
$C_{13}H_{20}O_7$. Calculated %: CH_3CO 44.76

Dihydro-4-hydroxy-2-(1-hydroxy-1-methylethyl)-3(2H)-furanone Diacetic Ester (VI)

A mixture of 10 g of the keto diepoxide (II), 34 g of glacial acetic acid, and 26 g of freshly distilled acetic anhydride was heated in a sealed glass tube at 150° for two hours. Excess of acetic acid and acetic anhydride was distilled off. Vacuum distillation of the residue gave 11 g of a substance of b.p. 120-130° (1 mm), and from this, by repeated fractionation, 5.5 g of the diacetic ester (VI) was isolated as a yellow viscous sirup, b.p. 131-132° (2 mm); n_D^{20} 1.4525; d_4^{20} 1.1717; found MR 56.28; calculated MR 55.58.

Found %: C 54.17; 54.10; H 6.41; 6.50
$C_{11}H_{16}O_6$. Calculated %: C 54.09; H 6.60

Found: M 243.4; 240.8 (in benzene)
$C_{11}H_{16}O_6$. Calculated: M 244

Found %: CH_3CO 36.1; 35.92;
$C_{11}H_{16}O_6$. Calculated %: CH_3CO 35.22

The diacetic ester (V) does not contain free hydroxy groups. It gives a 2,4-dinitrophenylhydrazone, but we did not succeed in recrystallizing it.

2-(1-Methoxy-1-methylethyl)-3(2H)-furanone (VII)

A solution of 5 g of the keto diepoxide (II) in 60 ml of methanol was heated in a closed metal tube at 250° for one hour. Methanol was distilled off, and the residue was vacuum-fractionated. Three experiments carried out under similar conditions gave 9.3 g of a viscous orange liquid, b.p. 112-125° (7.5 mm). When allowed to stand, the liquid partially crystallized; the crystals were filtered off. Recrystallization from hexane gave 3 g of 2-(1-methoxy-1-methylethyl)-3(2H)-furanone (VII) in the form of colorless needles, m.p. 125-126°. The high value of the molecular weight in benzene (see below) is probably to be explained by the association of the compound (VII) with benzene.

Found %: C 61.54; 61.72; H 7.79; 7.82
$C_8H_{12}O_3$. Calculated %: C 61.52; H 7.74

Found %: OCH_3 20.28; 20.08
$C_8H_{12}O_3$. Calculated %: OCH_3 19.87

Found: M 218.9; 219.9;(in benzene) 142.7; 140.5 (in dioxane)
$C_8H_{12}O_3$. Calculated: M 156

Found %: OH 13.69; 13.89 (in pyridine)
$C_8H_{11}O_2(OH)$ (enol) Calculated %: OH 10.88

The compound (VII) did not undergo hydrogenation in presence of Raney nickel, platinum, or palladium at room temperature. It gave a dark-blue color with ferric chloride solution. It did not react with diazomethane. It decolorized potassium permanganate solution. It gave a 2,4-dinitrophenylhydrazone, which we did not succeed in recrystallizing. In bromination with bromine in chloroform or glacial acetic acid, hydrogen bromide was evolved.

After refractionation under reduced pressure, the liquid product remaining after separation of the crystals gave 4.5 g of a substance of b.p. 93-94° (3 mm), n_D^{20} 1.4960; d_4^{20} 1.1195, which partially crystallized on standing and gave the substance (VII), m.p. 125-126°.

Found %: C 58.9; 58.72; H 7.45; 7.47
$C_8H_{12}O_3$. Calculated %: C 61.52; H 7.74

Found: M 220.5; 221.6; (in benzene) 141; 138.4 (in dioxane)
$C_8H_{12}O_3$. Calculated: M 156

Found %: OH 13.71; 13.6 (in pyridine)
$C_8H_{12}O_3$. (enol) Calculated %: OH 10.88

The liquid product gave a dark-green color with aqueous ferric chloride. In its behavior toward potassium permanganate solution, 2,4-dinitrophenylhydrazine, and bromine it resembled the solid product (VII).

Preparation of 2-(1-Ethoxy-1-methylethyl)-3(2H)-furanone (VIII)

By reaction under similar conditions, 20 g of the keto diepoxide (II) and 240 ml of ethanol (in four experiments) gave two products: 12.7 g, b.p. 104-113° (3.5 mm), n_D^{14} 1.4622 and 2.8 g, b.p. 113-131° (3.5 mm). From these, by dissolution in distilled water, we isolated 2 g of 2-(1-ethoxy-1-methylethyl)-3(2H)-furanone (VIII) in the form of colorless crystals, m.p. 116-117° (from hexane).

Found %: C 63.51; 63.71; H 8.33; 8.34
$C_9H_{14}O_3$. Calculated %: C 63.51 H 8.29

Found %: OC_2H_5 27.58
$C_9H_{14}O_3$. Calculated %: OC_2H_5 26.47

The 3(2H)-furanone (VIII) gave a dark-blue color with aqueous ferric chloride and decolorized permanganate solution. When bromine was added to its solution in chloroform or glacial acetic acid, liberation of hydrogen bromide was observed. The liquid product remaining after separation of the crystals was vacuum-fractionated and gave 8.0 g of a substance of b.p. 91-91.5° (2 mm), n_D^{20} 1.4672; d_4^{20} 1.0974

Found %: C 58.18; 58.06; H 8.34; 8.26
$C_9H_{14}O_3$. Calculated %: C 63.51; H 8.29

Found: M 208; 210.1 (in benzene); 154; 152.2 (in dioxane)
$C_9H_{14}O_3$. Calculated: M 170

Found %: OH 12.28; 12.19 (in pyridine)
$C_9H_{13}O_2(OH)$ (enol) Calculated %: OH 10.0

With aqueous ferric chloride it gave a dark-green coloration.

Preparation of 2-(1-Isopropoxy-1-methylethyl)-3(2H)-furanone (IX)

A solution of 5 g of the keto diepoxide (II) in 60 ml of isopropyl alcohol was heated in an open metal tube for one hour at 240°. From three similar experiments we obtained, in all, 7.65 g of yellowish liquid of b.p. 100-120° (3 mm), from which, by dilution with water, we isolated 1 g of 2-(1-isopropoxy-1-methylethyl)-3(2H)-furanone (IX) in the form of colorless crystals, m.p. 128.5-129° (from hexane).

Found %: C 65.49; 65.50; H 8.95; 8.98
$C_{10}H_{16}O_3$. Calculated %: C 65.2 H 8.74;

Found: M 234.7; 234.3 (in benzene)
$C_{10}H_{16}O_3$. Calculated: M 184.2

The 3(2H)-furanone (IX) gave a dark-blue color with aqueous ferric chloride.

Hydrogenation of the Keto Diepoxide (II)

The keto diepoxide (II) (10 g), as a solution in 30 ml of ethanol, was hydrogenated at room temperature in presence of 1 g of Raney nickel. In the course of 38 hours, 3.16 liters of hydrogen (2 molecular proportions) was absorbed. The catalyst was removed, and the residue was twice fractionated under reduced pressure. The product, amounting to 3 g, was dihydro-2-isopropyl-3(2H)-furanone (XI), a mobile liquid having b.p. 166– 166.5° (737 mm); 74.5 – 74.75° (20 mm); n_D^{20} 1.4252; d_4^{20} 0.9551; found MR 34.35; calculated MR 33.98.

Found %: C 65.5; 65.5; H 9.67; 9.71
$C_7H_{12}O_2$. Calculated %: C 65.58; H 9.43

Found: M 124.2; 124.2 (in benzene)
$C_7H_{12}O_2$. Calculated: M 128

Its semicarbazone melted at 127-128° (from a mixture of acetone and hexane)

Found %: N 22.19; 22.16
$C_8H_{15}O_2N_3$. Calculated %: N 22.69

The dihydro-3(2H)-furanone (XI) does not contain hydroxy groups. Apart from (XI), in this experiment we isolated about 3.5 g of dihydro-4-hydroxy-2-isopropyl-3(2H)-furanone (X) in the form of a viscous liquid, b.p. 97 – 98° (1.5 mm); n_D^{20} 1.4570; d_4^{20} 1.1015; found MR 35.65; calculated MR 35.5

Found %: C 58.1; 58.0; H 8.54; 8.48
$C_7H_{12}O_3$. Calculated %: C 58.3; H 8.39

Found: M 148.3; 146.2
$C_7H_{12}O_3$. Calculated: M 144

Found %: OH 11.19; 11.13
$C_7H_{11}O_2(OH)$. Calculated %: OH 11.79

Its semicarbazone melted at 186.5° with decomposition (from absolute alcohol).

Found %: N 20.89; 21.04
$C_8H_{15}O_3N_3$. Calculated %: N 20.88

The dihydrohydroxy-3(2H)-furanone (X) did not undergo hydrogenation in presence of Raney nickel at room temperature. A similar result was obtained in the hydrogenation of the keto diepoxide (II) at room temperature in presence of Raney nickel for 8 hours 30 minutes with the absorption of only one molecular proportion of hydrogen. In this experiment, from 10 g of the keto diepoxide (II) – 2g of (X), 2.5 g of (XI), and 2.5 g of the original keto diepoxide (II) were obtained.

Preparation of Dihydro-4-hydroxy-2-(1-methyl-1-piperidinoethyl)-3(2H)-furanone (XIV)

The keto diepoxide (II) (2 g) was added to a solution of 1.4 g of piperidine in an equal amount of distilled water. Reaction proceeded with evolution of heat: in three minutes the temperature of the mixture rose from 20° to 60°. By periodic cooling with ice water the temperature of the mixture was maintained at not above 60°. An oil formed at the botton of the flask, and in the course of 20 minutes it completely solidified. The crystals were filtered off and washed three times with water. Recrystallization from 50% aqueous methanol gave 1.9 g of dihydro-4-hydroxy-2-(1-methyl-1-piperidinoethyl)-3(2H)-furanone (XIV) in the form of colorless crystals, m.p. 85-86°

Found %: C 63.34; 63.39; H 9.24; 9.32; N 6.22; 6.10
$C_{12}H_{21}O_3N$. Calculated %: C 63.40; H 9.31; N 6.16

The methiodide was prepared by heating (XIV) with excess of methyl iodide at 50-55° for eight hours. It melted with decomposition at 158-159° (from acetone).

Found %: N 3.57; 3.52
$C_{13}H_{24}O_3NI$. Calculated %: N 3.79

Dry hydrogen chloride was passed for 30 minutes through a solution of 0.2 g of (XIV) in 30 ml of absolute ether cooled with ice water; 0.07 g of piperidine hydrochloride, m.p. 242.5-243.5° (from a mixture of alcohol and ether), was obtained; there was no depression of melting point in a mixture test with a known sample. Treatment of 0.5 g of (XIV) with an alcoholic solution of 0.5 g of picric acid gave 0.25 g of piperidine picrate, m.p. 149-150° (from absolute alcohol), undepressed by admixture of a known sample.

Preparation of 2-(1-Methyl-1-piperidinoethyl)-3(2H)-furanone (XV)

A mixture of 7 g of (XIV) and 28 g of acetic anhydride was allowed to stand at room temperature for two hours. The usual treatment gave 3.8 g of 2-(1-methyl-1-piperidinoethyl)-3(2H)-furanone (XV), b.p. 131.5° (3 mm) and n_D^{20} 1.5738

Found %: C 68.68; 68.86; H 9.04; 9.25
$C_{12}H_{19}O_2N$. Calculated %: C 68.85; H 9.15

Its methiodide melted with decomposition at 134-135° (from a mixture of acetone and dry ether).

Found %: N 3.69; 3.64
$C_{13}H_{22}O_2NI$. Calculated %: N 3.98

In the treatment of (XV) with hydrogen chloride, we isolated piperidine hydrochloride, m.p. 243-243.5°, undepressed by admixture of a known sample. Treatment of (XV) with picric acid gave piperidine picrate, m.p. 149-150°, undepressed by admixture of a known sample.

Preparation of Tetrahydro-2-(1-methyl-1-piperidinoethyl)-3-phenyl-3,4-furandiol (XVI)

A mixture of 5.3 g of fine lithium turnings and 150 ml of dry ether was prepared in a three-necked flask fitted with mercury-sealed stirrer, reflux condenser protected with a calcium chloride tube, dropping funnel, and tube for the passage of nitrogen. Bromobenzene (2 g) was added, and after reaction had set in, a solution of 50 g of bromobenzene in 100 ml of dry ether was added over a period of 2 hours 20 minutes, the addition being carried out at the boiling point of ether. The reaction mixture was then boiled for a further one hour.

A solution of 15 g of (XIV) in 100 ml of dry ether was then added dropwise over a period of 1 hour 40 minutes to the above preparation of phenyllithium at a bath temperature of − 10°. The mixture was stirred at room temperature for one hour and then set aside overnight at room temperature. On the next day the mixture was heated at the boiling point of ether for three hours. It was then cooled, and was decomposed with 80 ml of distilled water. A crystalline precipitate formed, and this was filtered off and washed on the filter with ether and water. Recrystallization from methanol gave 15.8 g of tetrahydro-2-(1-methyl-1-piperidinoethyl)-3-phenyl-3,4-furandiol (XVI) in the form of colorless crystals, m.p. 169-170°.

	Found %:	C 70.88;	70.89;	H 8.60;	8.62;	N 4.59;	4.82
$C_{18}H_{27}O_3N$.	Calculated %:	C 70.79;		H 8.91;		N 4.58	

Treatment of (XVI) with hydrogen chloride gave a substance of m.p. 240.5-241.5°, undepressed by admixture of piperidine hydrochloride. The same piperidine hydrochloride, m.p. 240-241°, was obtained by the action propionyl chloride on (XVI). The expected propionic ester was not obtained.

Preparation of 2-(1-Diethylamino-1-methylethyl)dihydro-4-hydroxy-3(2H)-furanone (XVII)

The keto diepoxide (II) (7 g) was added over a period of three minutes to a solution of 4.2 g of diethylamine in an equal volume of water at 13°. By cooling with water the temperature of the reaction mixture was maintained at not above 30° for two hours. When heat was no longer evolved, the mixture was kept for two hours at room temperature and the oil that separated was extracted with ether. The ether extract was dried with sodium sulfate and vacuum-distilled. The product, amounting to 5.8 g, was 2-(1-diethylamino-1-methylethyl)-dihydro-4-hydroxy-3(2H)-furanone (XVII), a viscous orange liquid, b.p. 124° (3 mm) and n_D^{20} 1.5472

	Found %:	C 61.33;	61.25;	H 9.66;	9.81;	N 6.35;	6.31
$C_{11}H_{21}O_3N$.	Calculated %:	C 61.36;		H 9.83;		N 6.50	

When (XVII) was treated with hydrogen chloride, a product of m.p. 231-231.5° was obtained, and this showed no depression of melting point in admixture with diethylamine hydrochloride. An attempt to prepare a crystalline methiodide of (XVII) was not successful: a noncrystallizing oil was obtained.

Preparation of 2-(1-Diethylamino-1-methylethyl)tetrahydro-3-phenyl-3,4-furandiol (XVIII)

The procedure was as described above for the synthesis of (XVI). Reaction between 7 g of (XVII) and phenyllithium prepared from 2.24 g of lithium and 136 g of bromobenzene gave 6.45 g of 2-(1-diethylamino--1-methylethyl)tetrahydro-3-phenyl-3,4-furandiol (XVIII) in the form of colorless crystals, m.p. 122.5-123.5°.

	Found %:	C 69.75;	69.87;	H 9.58;	9.46;	N 4.56;	4.71
$C_{17}H_{27}O_3N$.	Calculated %:	C 69.60;		H 9.27;		N 4.77	

Preparation of 2-(1-Dimethylamino-1-methylethyl)dihydro-4-hydroxy-3(2H)-furanone (XIX)

The keto diepoxide (II) (3 g) was added at room temperature to 3.2 g of 30% aqueous dimethylamine. In three minutes the temperature of the mixture reached 52°, and it was maintained at this value by cooling the flask with ice water. When the exothermic reaction stopped, the cooled solution was extracted with ether, and the extract was dried with sodium sulfate. Ether was distilled off, and heating of the residue with petroleum ether enabled us to isolate 1.5 g of crystals, m.p. 73-74.5°. Recrystallization from dry ether gave 2-(1-dimethylamino-1-methylethyl)-dihydro-4-hydroxy-3(2H)-furanone (XIX) in the form of colorless crystals, m.p. 74-75°.

Found %: C 57.89; 58.18; H 9.35; 9.03; N 7.32; 7.21
$C_9H_{17}O_3N$. Calculated %: C 57.72; H 9.15 N 7.47

Preparation of 2-(1-Dimethylamino-1-methylethyl)tetrahydro-3-phenyl-3,4-furandiol (XX)

The procedure was as described above for the synthesis of (XVI). Reaction between 3.5 g of (XIX) and phenyllithium prepared from 1.3 g of lithium and 10.8 g of bromobenzene gave 1.5 g of 2-(1-dimethylamino--1-methylethyl)tetrahydro-3-phenyl-3,4-furandiol (XX) in the form of colorless crystals, m.p. 148-149° (from alcohol).

Found %: C 67.63; 67.44; H 8.70; 8.57; N 5.52 5.25
$C_{15}H_{23}O_3N$. Calculated %: C 67.92; H 8.74; N 5.28

Action of Anhydrous Zinc Chloride on the Keto Diepoxide (II)

A mixture of 4 g of fused zinc chloride and 80 ml of dry ether was prepared in a three-necked flask fitted with mechanical stirrer and reflux condenser, and 4 g of the keto diepoxide (II) was added with vigorous stirring. The mixture was stirred at the boiling point of ether for three hours. The reaction mixture was cooled and treated with 10 ml of water. The precipitate was filtered off and washed with water and ether. The ether layer was separated and dried with magnesium sulfate. Three experiments carried out under similar conditions gave about 6 g of a viscous orange liquid, which darkened in color when allowed to stand in a desiccator over phosphoric oxide. It had b.p. 86.5° (1.5 mm), n_D^{20} 1.4738; d_4^{20} 1.2339; it appeared to contain the tricarbonyl compound (XXI).

Found %: C 49.09; 49.17; H 6.98; 6.78
$C_7H_{10}O_3 \cdot H_2O$. Calculated%: C 52.5; H 7.5

Found: M 200.1; 199.8 (in benzene); 198; 193.8 (in dioxane)
Calculated: M 160

Found %: OH 13.73; 13.65
$C_7H_{10}O_3 \cdot H_2O$. Calculated %: OH 19.1

The substance did not contain zinc, and it gave a 2,4-dinitrophenylhydrazone, m.p. 146-146.5° (decomposition), which we did not succeed in recrystallizing.

Found %: C 47.95; 47.95; H 4.21; 4.11; N 15.15; 14.96

The product did not give the enol test with aqueous $FeCl_3$; it did not contain chlorine, and it had a neutral reaction. When distilled over phosphoric oxide and silica gel, it was partly recovered unchanged (b.p. 86.5°/1.5 mm) and partly converted into polymer.

When recrystallized from 86% acetic acid, the precipitate formed in the reaction mixture on dilution with water gave 4.5 g of colorless glistening prisms, m.p. 250-251° (decomposition).

Found %: C 22.59; 22.65; H 4.68; 4.56; Zn 30.13; 30.18

The presence of zinc was confirmed also by spectrum analysis. In the spectrum of this compound, the following zinc lines were found: 3302.06, 4722.2, and 4810.5 A.

The semicarbazone of this compound melted with decomposition at 195-196° (from a mixture of ether and acetic acid).

Found %: C 23.38; 23.38; H 4.31; 4.18; N 15.53; 15.30; Zn 24.51; 24.64

The product did not contain chlorine, and it was readily soluble in water and methanol, less soluble in ethanol, and insoluble in ether, benzene, dioxane, and acetone. When hydrogen sulfide was passed through an aqueous or acetic acid solution of the product, a white precipitate of zinc sulfide formed.

SUMMARY

1. The reactions of the keto diepoxide (II) with acetic acid, alcohols, and secondary amines were studied. Some new ketones of the furan series were described, and by the action of phenyllithium on these the corresponding phenyl-substituted alcohols were prepared.

2. Catalytic hydrogenation of the keto diepoxide (II) in presence of Raney nickel gave the dihydro-3-(2H)-furanone (XI) and the dihydrohydroxy-3(2H)-furanone (X).

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COMMUNICATION 16. STEREOCHEMISTRY OF THE DIENE CONDENSATION OF CYCLOPENTADIENE WITH CITRACONIC ANHYDRIDE AND STERIC TRANSFORMATIONS OF THE ENDO AND EXO ADDUCTS

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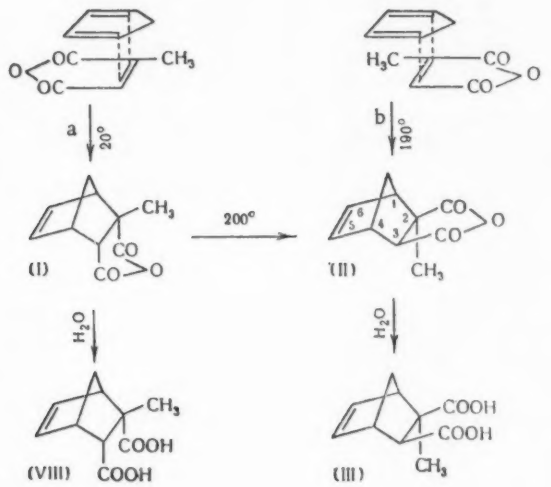
It is known that diene condensations of cyclopentadiene with maleic anhydride and its homologs at low temperatures proceed mainly with formation of adducts of the endo type in accordance with the scheme (a) which corresponds to the rule of "accumulation of unsaturation" [1-6]. However, in the study of diene condensations with various fulvenes it was shown that this reaction may proceed in both possible steric directions, the relative amounts of the stereoisomers being dependent on temperature [1, 7, 8]. A similar relationship between the steric direction of a diene reaction and temperature was established also for the condensation of cyclopentadiene with maleic anhydride [9] and was studied in detail by us for the condensations of 1-vinyl-1-cyclohexene with maleic anhydride [10] and methyl acrylate [11].

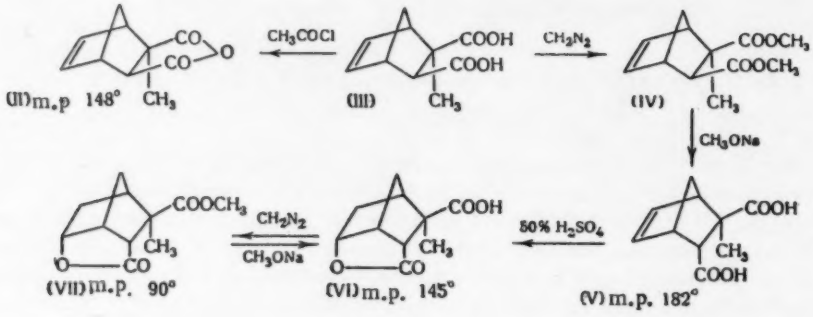
In continuation of our study of the stereochemistry of the diene synthesis, in the present investigation we have studied the condensation of cyclopentadiene with citraconic anhydride at 190-195°. It was found that, under these conditions, the product was a mixture of endo and exo anhydrides (I) and (II), from which, by distillation, hydrolysis, and crystallization, we succeeded in isolating the pure exo acid (III) in a yield of about 30%. This acid was obtained in similar yield by heating the endo anhydride (I) [2] to 200°, a change that was accompanied by partial dissociation of the original anhydride into the original components of (II).



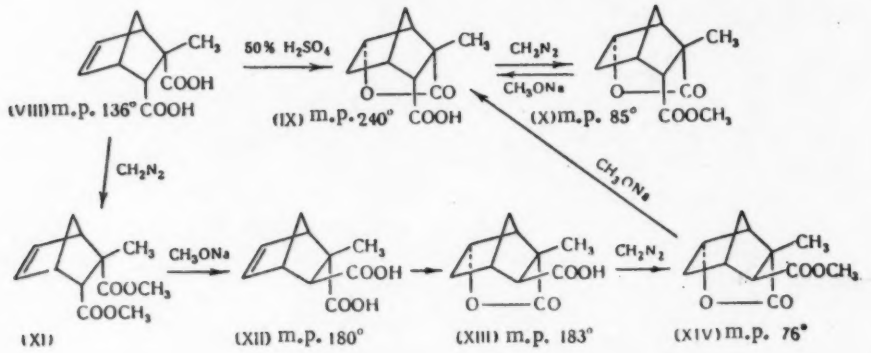
These results show that, at high temperatures, the condensation of cyclopentadiene with citraconic

anhydride proceeds with violation of the principle of "accumulation of unsaturation" and follows the scheme (b) which results in the formation of the exo adduct (II).

The configurations of the stereoisomeric anhydrides (I) and (II) were proved rigorously in a study of the lactonization and mutual steric transformations of the corresponding acids. In accord with its exo structure, 2-methylbicyclo[2.2.1]hept-5-ene-2,3-exo-cis-dicarboxylic acid (III) was found to be incapable of lactonization, and by isomerization of the corresponding exo diester (IV) with sodium methoxide it gave the trans acid (V) having the secondary carboxyl in the endo position. The trans acid (V) has been recently prepared by Alder [6] by the condensation of cyclopentadiene with mesaconoyl chloride. When heated with 50% sulfuric acid, the trans acid (V) was readily lactonized to the trans γ-lactone acid (VI) at the secondary endo carboxyl, so that the corresponding trans γ-lactone ester (VII) was incapable of being isomerized by sodium methoxide. The infrared spectrum of the γ-lactone ester (VII) contains a carbonyl absorption band at 5.60 μ, which is characteristic for γ-lactones [12].

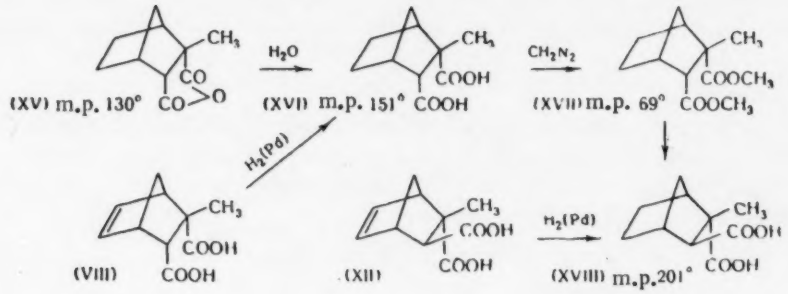


The isomeric endo acid (VIII) behaved differently. Because of the endo positions of both carboxyls it was readily lactonized by 50 % sulfuric acid with formation of the cis γ-lactone acid (IX), which gave the cis γ-lactone ester (X), a substance that was incapable of being isomerized by sodium methoxide. Isomerization of the endo diester (XI) readily gave the new trans acid (XII) having the methyl and secondary carboxyl in exo positions. This trans acid (XII) can be lactonized only with participation of the tertiary endo carboxyl, and it then gives the isomeric trans γ-lactone acid (XIII), which gives the γ-lactone ester (XIV), m.p. 76°, with diazomethane. The isomeric γ-lactone ester (X) and (XIV) give carbonyl absorption bands at 5.63 and 5.60 μ, corresponding to the presence of a γ-lactone ring, and they differ only in the spatial disposition of the secondary methoxycarbonyl group, this being proved by isomerization of the γ-lactone ester (XIV) into the γ-lactone acid (IX).

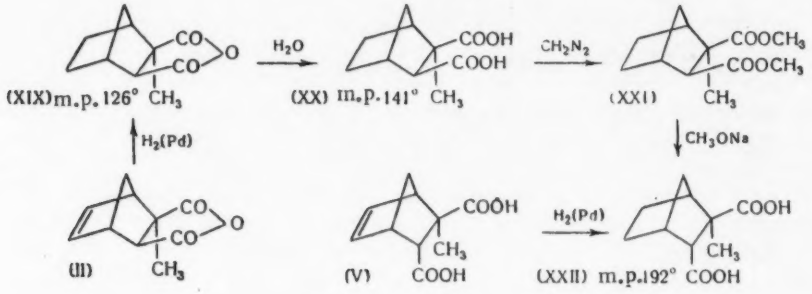


Our results show that, in spite of the endo positions of both carboxyls of the endo acid (VIII), its lactonization proceeds only at the tertiary carboxyl, the more stable product being the γ-lactone acid (IX), in which the methyl and carboxy groups have a trans arrangement.

The configurations of all four isomeric 2-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids (III), (V), (VIII), and (XII) were confirmed also by studying the mutual transformations of the corresponding saturated acids and their derivatives. It was found that the saturated endo cis acid (XVI), which is readily prepared by hydrolysis of the endo cis anhydride (XV) or by hydrogenation of the endo cis acid (VIII), can be converted, through the isomerization of its ester (XVII) with sodium methoxide, into the saturated trans acid (XVIII) with the secondary carboxyl in the exo position. This trans acid is obtained also by hydrogenation of the unsaturated trans acid (XII).



Similarly, the saturated exo cis anhydride (XIX), obtained by hydrogenation of the exo cis anhydride (II), is hydrolyzed to the saturated exo cis acid (XX), which forms the exo cis diester (XXI) with diazomethane. The last compound, via isomerization with sodium methoxide, is readily converted into the isomeric trans acid (XXII), which can be obtained also by hydrogenation of the trans acid (V).



In this way we prepared all four isomeric 2-methylbicyclo[2.2.1]heptane-2,3-dicarboxylic acids (XVI), XVIII), (XX), and (XXII) and proved their spatial configurations.

The condensation of cyclopentadiene with dimethyl mesaconate was investigated, and it was found that this reaction, unlike the condensation with mesaconoyl chloride [6], gives a mixture of the isomeric trans acids (V) and (XII) (in almost equal proportions), the separation of which is very difficult owing to their similar solubilities.

EXPERIMENTAL

2-Methylbicyclo[2.2.1]hept-5-ene-2,3-exo-cis-dicarboxylic acid (III)

a) A mixture of 16.8 g of citraconic anhydride, 10.4 g of cyclopentadiene dimer, and 30 ml of dry benzene was heated in a closed steel tube at 190-195° for two hours. Vacuum fractionation gave 14.3 g of adduct, b.p. 120-135° (6 mm), which solidified almost completely when cool. The adduct was pressed off on a filter funnel to remove the small amount of liquid, and it was hydrolyzed at the boil with 70 ml of 10% sodium hydroxide solution. The alkaline solution was treated with charcoal and filtered. Acidification with hydrochloric acid gave 11 g of the exo acid (III), m.p. 141-143°. After two crystallizations from 5 : 1 water–acetone, the exo acid (III) melted constantly at 149-150°.

Found %: C 61.23; 61.17; H 6.35; 6.26

$C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.17

b) The endo cis anhydride (I) (7 g; m.p. 138°) [5] was heated in a stream of nitrogen at 200° for one hour, and the reaction product was vacuum-distilled. Two fractions were obtained: Fraction I (1.1 g), b.p. 100-120° (8 mm), and Fraction II (3.1 g), b.p. 120-135° (6 mm).

After hydrolysis with a little water, Fraction I gave 0.6 g of citraconic acid, m.p. 92-93°, undepressed by admixture of a known sample. After hydrolysis with 10% sodium hydroxide and crystallization, Fraction II gave 1.9 g of the exo acid (III), m.p. 148-149°, undepressed by admixture of the sample described above.

exo cis Anhydride (II)

A mixture of 1.5 g of the exo cis acid (III) and 15 ml of acetyl chloride was boiled for one hour. Volatile material was distilled off under reduced pressure, and the residue crystallized when treated with petroleum ether. The product (1.3 g) was the exo cis anhydride (II), which melted constantly at 147-148° after crystallization from a mixture of petroleum ether and benzene.

Found %: C 66.94; 67.07; H 5.76; 5.65

$C_{10}H_{10}O_3$. Calculated %: C 67.30; H 5.66

exo cis Diester (IV)

A suspension of 4.8 g of the exo cis acid (III) in ether was treated with excess of ethereal diazomethane. Vacuum distillation gave 4.6 g of the exo cis diester (IV), b.p. 108° (5 mm); n_D^{20} 1.4820; d_4^{20} 1.1447; found MR 55.85; calculated MR 56.06

Found %: C 64.32; 64.21; H 7.21; 7.13

$C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19

2-endo-Methylbicyclo[2.2.1]hept-5-ene-2,3-trans-dicarboxylic Acid (V)

The exo cis diester (IV) (6 g) was added to a solution of 17 g of sodium in 300 ml of absolute methanol, and the mixture was boiled for 20 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in the minimum amount of water and boiled for two hours. Water was added until the precipitate present had dissolved, and the resulting solution was treated with charcoal, filtered, and acidified with hydrochloric acid. Crystals of m.p. 162-165° (4 g) were obtained, and crystallization of these from aqueous acetone gave 3.2 g of pure trans acid (V), m.p. 181-182°. The yield was 60%. The trans acid (V) obtained by Alder [6] melted at 170-171°.

Found %: C 61.31; 61.39; H 6.17; 6.26

$C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.17

By treatment with diazomethane, the trans acid (V) was converted into its diester, b.p. 114-115° (6 mm); n_D^{20} 1.4830; d_4^{20} 1.1460; found MR 55.90; calculated MR 56.06

Found %: C 64.23; 64.13; H 7.19; 7.37

$C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19

endo cis Diester (XI)

A suspension of 8 g of the endo cis acid (VII) [6] in ether was treated with ethereal diazomethane. Distillation gave 8.5 g of the endo cis diester (XI), b.p. 112° (4 mm); n_D^{20} 1.4850; d_4^{20} 1.1504; found MR 55.90; calculated MR 56.06

Found %: C 64.42; 64.38; H 7.14; 6.91

$C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19

2-exo-Methylbicyclo [2.2.1] hept-5-ene-2,3-trans-dicarboxylic Acid (XII)

The endo cis diester (XI) (10 g) was added to a solution of 13 g of sodium in 600 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, 70 ml of water was added, boiling was continued for a further two hours, and the solution was evaporated to low bulk in a porcelain dish on a water bath. The precipitate of salts was filtered off and dissolved in water, and the solution was acidified with hydrochloric acid. The product (7 g) was the trans acid (XII), m.p. 179-180°, not raised by crystallization from aqueous acetone, but depressed by admixture with the isomeric trans acid (V) (the mixture melted at 163-165°). The trans acid (XII) prepared by Alder melted at 185°.

Treatment of the trans acid (XII) with diazomethane gave the diester, b.p. 104° (3 mm); n_D^{20} 1.4820; d_4^{20} 1.1469; found MR 56.07; calculated MR 56.06

	Found %:	C 64.09;	63.99;	H 7.29; 7.34
$C_{12}H_{16}O_4$	Calculated %:	C 64.27;		H 6.19

trans γ-Lactone Acid (VI)

A mixture of 2 g of the trans acid (V) and 20 ml of 50% sulfuric acid was stirred vigorously at 60° for two hours. The solution was diluted with an equal volume of water and cooled, when 1.5 g of the trans γ-lactone acid (VI) separated. After crystallization from water containing a little acetone it melted constantly at 144-145°.

	Found %:	C 61.22;	61.31;	H 6.14; 6.17
$C_{10}H_{12}O_4$	Calculated %:	C 61.21;		H 6.17

Titration with alkali showed that the trans γ-lactone acid (VI) contained one free carboxy group.

trans γ-Lactone Ester (VII)

Treatment of 1.3 g of the trans γ-lactone acid (VI) with diazomethane gave 1.3 g of the trans γ-lactone ester (VII), which melted at 89-90° after crystallization from a 2 : 1 mixture of diethyl ether and petroleum ether.

	Found %:	C 62.56;	62.74;	H 6.62; 6.73
$C_{11}H_{14}O_4$	Calculated %:	C 62.85;		H 6.72

When the trans γ-lactone ester (VII) was boiled with 10% sodium methoxide, the original trans γ-lactone acid (VI) was isolated quantitatively.

cis γ-Lactone Acid (IX)

A mixture of 5 g of the endo cis acid (VIII) [5] and 50 ml of 50% sulfuric acid was stirred at 60° for two hours; the solution was diluted with an equal volume of water and cooled. The product (3.5 g) was the cis γ-lactone acid (IX), m.p. 233-235°. After being crystallized from 40% acetone it melted at 240°. Titration showed that it contained only one carboxy group.

	Found %:	C 61.25;	61.41;	H 6.18; 6.17
$C_{10}H_{12}O_4$	Calculated %:	C 61.21;		H 6.17

Treatment with diazomethane gave a quantitative yield of the cis γ-lactone ester (X), m.p. 84-85° (from ether).

	Found %:	C 62.95;	62.72;	H 6.76; 6.69
$C_{11}H_{14}O_4$	Calculated %:	C 62.85;		H 6.72

When an attempt was made to isomerize the cis γ-lactone ester (X) by boiling it with sodium methoxide, the only individual product isolated was the original cis γ-lactone acid (IX), obtained in a yield of about 50%

trans γ-Lactone Acid (XIII)

A mixture of 2.5 g of the trans acid (XII) and 25 ml of 50 % sulfuric acid was stirred at 60° for 90 minutes

and then at 100° for 30 minutes. The solution was diluted with an equal volume of water and cooled, when 1.75 g of crystals, m.p. 177-179°, gradually separated. Crystallization from water containing a little acetone gave 1.5 g of the trans γ-lactone acid (XIII), m.p. 182-183°, depressed by admixture of the original trans acid (XII). Titration showed that it contained one free carboxy group.

Found %: C 61.28; 61.19; H 6.27; 6.21
$C_{10}H_{12}O_4$. Calculated %: C 61.21; H 6.17

trans γ-Lactone Ester (XIV)

A suspension of 1.8 g of the trans γ-lactone acid (XIII) in ether was treated with excess of ethereal diazomethane. The solution was evaporated down to low bulk, and 1.7 g of the trans γ-lactone ester (XIV) was obtained. After crystallization from ether it melted at 75-76°.

Found %: C 63.03; 62.79; H 6.75; 6.60
$C_{11}H_{14}O_4$. Calculated %: C 62.85; H 6.72

Isomerization of the trans γ-Lactone Ester (XIV)

The trans γ-lactone ester (XIV) (1.4 g) was added to a solution of 3.5 g of sodium in 90 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, the residue was dissolved in 20 ml of water, and the resulting solution was boiled for two hours, filtered, and evaporated to low bulk. The precipitate of salts was filtered off and dissolved in water. Acidification gave 0.9 g of crystals, m.p. 224-227°, which melted at 238-240° after crystallization from 50% acetone. There was no depression of melting point in a mixture test with the above-described cis γ-lactone acid (IX).

2-Methylbicyclo[2.2.1]heptane-2,3-endo-cis-dicarboxylic Acid (XVI)

a) The endo cis anhydride (I) [2] (4 g), as a solution in 60 ml of dry benzene, was hydrogenated over a palladium catalyst, and one molecular proportion (500 ml) of hydrogen was absorbed. Catalyst was filtered off, benzene was distilled off under reduced pressure, and in this way we obtained 3.8 g of the saturated endo cis anhydride (XV), m.p. 127-128°, which is in accord with data in the literature [6]. Hydrolysis of this anhydride with 10% sodium hydroxide solution gave a quantitative yield of the saturated endo cis acid (XVI), which was vacuum-dried and then had m.p. 151-152°, which is in accord with data in the literature [6].

b) The endo cis acid (VIII) [6] (2 g), as a solution in 50 ml of absolute methanol, was hydrogenated over a palladium catalyst, and one molecular proportion of hydrogen was absorbed. Methanol was distilled off, and crystallization of the residue from aqueous acetone gave 1.5 g of the saturated endo cis acid (XVI), m.p. 150-151°, undepressed by admixture with the sample obtained in the preceding experiment.

Saturated endo cis Diester (XVII)

A suspension of 3.5 g of the endo cis acid (XVI) in ether was treated with ethereal diazomethane. Ether was distilled off, and the residue crystallized when treated with petroleum ether. The product (3.2 g) was the saturated endo cis diester (XVII), m.p. 68-69° after crystallization from petroleum ether. The endo cis diester (XVII) obtained by Alder [6] melted at 63-64°

Found %: C 63.92; 64.07; H 8.21; 8.14
$C_{12}H_{18}O_4$. Calculated %: C 63.70; H 8.02

2-exo-Methylbicyclo[2.2.1]heptane-2,3-trans-dicarboxylic Acid (XVIII)

a) The saturated endo cis diester (XVII) (2.5 g) was added to a solution of 6 g of sodium in 150 ml of abolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, 40 ml of water was added, and the solution was boiled for a further two hours, treated with charcoal and filtered, evaporated down to low bulk, and acidified with hydrochloric acid. The product (1.95 g) was the saturated trans acid (XVIII), m.p. 197-199°. After crystallization from 50% aqueous acetone it melted at 201-202°, which is in accord with data in the literature [6].

b) The trans acid (XII) (0.4 g), as a solution in 25 ml of methanol, was hydrogenated over a palladium

catalyst; one molecular proportion (40 ml) of hydrogen was absorbed. Removal of methanol and crystallization of the residue from aqueous acetone gave 0.3 g of the saturated trans acid (XVIII), m.p. 199-201°, undepressed by admixture of sample obtained in the preceding experiment.

When treated with diazomethane, the saturated trans acid (XVIII) gave the corresponding diester, b.p. 111° (4 mm); n_D^{20} 1.4747; d_4^{20} 1.1302; found MR 56.33; calculated MR 56.53

	Found %:	C 63.81; 63.73;	H 7.91; 7.87
$C_{12}H_{18}O_4$.	Calculated %:	C 63.70;	H 8.02

Saturated exo cis Anhydride (XIX)

The exo anhydride (II) (5 g), as a solution in 100 ml of dry benzene, was hydrogenated over a palladium catalyst; one molecular proportion (600 ml) of hydrogen was absorbed. Benzene was distilled off, and the crystalline residue was recrystallized from petroleum ether. The product (4.2 g) was pure saturated exo cis anhydride (XIX), melting constantly at 125-126°.

	Found %:	C 66.91; 66.71;	H 6.74; 6.75
$C_{10}H_{12}O_3$.	Calculated %:	C 66.65;	H 6.71

Hydrolysis of the saturated exo cis anhydride (XIX) by boiling it with water gave the previously prepared [6] saturated exo cis acid (XX), m.p. 140-141° after crystallization from ether.

Saturated exo cis Diester (XXI)

The saturated exo cis acid (XX) (2.7 g) was treated with diazomethane. Distillation gave 2.4 g of the exo cis diester (XXI), b.p. 119° (6 mm); n_D^{20} 1.4780; d_4^{20} 1.1324; found MR 56.75; calculated MR 56.53

	Found %:	C 63.94; 64.04;	H 8.05; 7.93
$C_{12}H_{18}O_4$.	Calculated %:	C 63.70;	H 8.02

2-endo-Methylbicyclo[2.2.1]heptane-2,3-trans-dicarboxylic Acid (XXII)

a) The saturated exo cis diester (XXI) (2.3 g) was added to a solution of 6 g of sodium in 150 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off, the residue was dissolved in the minimum amount of water, and the resulting solution was boiled for a further two hours and acidified with hydrochloric acid. The product (1.3 g) was the saturated trans acid (XXII), m.p. 185-187°. Crystallization from 3 : 2 water-acetone raised the melting point to 191-192°, which is in accord with data in the literature [6]. When treated with diazomethane, the saturated trans acid (XXII) gave the corresponding diester, b.p. 116° (6 mm); n_D^{20} 1.4775; d_4^{20} 1.1343; found MR 56.40; calculated MR 56.53

	Found %:	C 63.53; 63.69;	H 8.08; 8.11
$C_{12}H_{18}O_4$.	Calculated %:	C 63.70;	H 8.02

b) The trans acid (V) (0.2 g), as a solution in 5 ml of methanol, was hydrogenated over a palladium catalyst. Solvent was distilled off, and the residue, crystallized from 40% acetone, gave 0.15 g of the saturated trans acid (XXII), m.p. 191-192°, undepressed by admixture of the sample obtained in the preceding experiment.

Condensation of Cyclopentadiene with Dimethyl Mesaconate

A mixture of 8 g of dimethyl mesaconate, 16.5 g (fivefold excess) of cyclopentadiene dimer, and 35 ml of dry benzene was heated in a closed steel tube for five hours at 190-200°. After removal of benzene and excess of cyclopentadiene dimer by distillation, the residue was vacuum-distilled and gave 10.2 g of adduct, b.p. 103-105° (4 mm), which contained some isomeric cyclopentadiene trimers as impurity. The product was hydrolyzed at the boil with 60 ml of 30% potassium hydroxide solution. The undissolved part was extracted with ether, and the alkaline solution was acidified with hydrochloric acid. The product (3.5 g) was a 1 : 1 mixture of the isomeric trans acids (V) and (XII), m.p. 164-166°. After three crystallizations from 30% aqueous acetone we were able to isolate only 0.1 g of pure trans acid (V), m.p. 181-182°.

SUMMARY

1. It was shown that the condensation of cyclopentadiene with citraconic anhydride at 190-195° proceeds in both possible steric directions and gives a mixture of the stereoisomeric endo and exo anhydrides (I) and (II), from which by hydrolysis it was found possible to isolate the exo acid (III) in a yield of about 30%.

2. The sterochemistry of the lactonization of the isomeric 2-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids was studied, and in this way the structure and configurations of the γ-lactone acids formed were proved.

3. All the theoretically possible steroisomers of 2-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (III), (V), (VIII), and (XII) were prepared, as also were the corresponding isomeric saturated acids (XVI), (XVIII), (XX), and (XXII), the configurations of which were established by their mutual stereospecific transformations.

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ORIENTATION IN THE CHLOROMETHYLATION REACTION

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We previously reported an investigation on orientation in the chloromethylation of toluene [1]. The present paper is concerned with the general question of orientation in chloromethylation, various aromatic compounds being taken as examples.

Although the view has been expressed that chloromethylation is an electrophilic-substitution reaction [2, 3], few known features of the reaction are peculiar to electrophilic substitution. The reaction mechaism – a very important criterion of reaction type – is not known: it has been suggested that chloromethylation proceeds by various mechanisms, depending on reaction conditions [2]. One feature characterizing the type of electrophilic-substitution reaction comprises the relationship obtaining between the yields of isomeric products – increase in the relative amount of meta isomer with rise in the electronegativity of the sutstituent and certain regularities observable in the ortho-para ratio.

For a long time there existed the view that chloromethylation of monosubstituted benzenes gives exclusively para derivatives [4]. It was later established that a mixture of isomers was formed in the chloromethylation of toluene [1] and benzyl chloride [5]. It is still considered that only para isomers are formed in the chloromethylation of chlorobenzenes [6]. The absence of attempts to investigate orientation in the chloromethylation reaction are evidently to be explained by the difficulties that are often met both in carrying out the reaction, and particularly in determining the composition of the mixture of isomeric products. The well known method of determining the relative amounts of isomers by thermal analysis is inapplicable to liquids, and spectroscopic determination requires pure standard specimens, which are not always available.

Apart from the previously described chloromethylation of toluene and investigation of the relative amounts of isomeric products, we carried out the chloromethylation of ethyl phenylacetate and benzyl chloride and the bischloromethylation of benzene. It was shown that the reaction products contained all three isomers. An attempt to chloromethylate benzoic acid and its methyl ester gave a very low yield (about 10%) of the meta derivative. For these cases the proportions of isomers were determined by the method developed previously, which consists in oxidation of the mixture of chloromethyl derivatives with dilute nitric acid at 200° [7] and separation of the benzenedicarboxylic acids formed [8]. The results show that, as in other cases of electrophilic substitution, with increase in the electronegativity of the substituent, the relative amount of m-(chloromethyl) derivative increases (Table 1).

Comparison of the results for the chloromethylation of toluene, ethylbenzene, cumene, and tert-butylbenzene showed the ortho-para ratio behaves in a strictly regular fashion. As we pass in this series from toluene to tert-butylbenzene, the relative amount of o-(chloromethyl) derivative greatly diminishes. This phenomenon, which is observed in known cases of electrophilic substitution, is undoubtedly associated with increased steric hindrance at the ortho position as we pass from toluene to tert-butylbenzene [3,9].

The chloromethylation of these hydrocarbons was carried out both in presence of anhydrous zinc chloride in nonpolar solvents (in excess of the hydrocarbon or in carbon tetrachloride) and also in a medium of concentrated hydrochloric acid in absence of zinc chloride; the relative amounts of isomers formed were found to be the same. The proportions of isomeric chloromethyl derivatives formed were determined by two methods. The first method consisted in the comparison of the amounts of terephthalic acid formed in the oxidation of the chloromethylation products with chromium trioxide in acetic acid: the results of the oxidation of the chloromethylation products from ethylbenzene and cumene were compared with the results of the oxidation

TABLE 1

Substance being chloromethylated	Composition of chloromethylation product (%)		
	para isomer	ortho isomer	meta isomer
$C_6H_5CH_3$	48.3	51.7	0
$C_6H_5CH_2COOC_2H_5$	60.4	27.0	12.6
$C_6H_5CH_2Cl$	69	16	15

TABLE 2

Substance being chloromethylated	Composition of chloromethylation product (%)	
	para isomer	ortho isomer
$C_6H_5CH_3$	48.3	51.7
$C_6H_5CH_2CH_3$	70	30
$C_6H_5CH(CH_3)_2$	85	15
$C_6H_5C(CH_3)_3$	100	0

of the mixture obtained in the chloromethylation of toluene, the composition of which has been rigorously established previously [1]. The results obtained by this method for the relative amounts of isomers obtained in the chloromethylation of toluene, ethylbenzene, and cumene are given in Table 2. However, this method was found to be unsuitable for determining the relative amounts of isomers formed in the chloromethylation of tert-butylbenzene, since in this case oxidation with chromium trioxide gives p-tert-butylbenzoic acid, and not terephthalic acid, which is formed in the oxidation of the chloromethyl derivatives of the other hydrocarbons. The second method of determining the relative amounts of isomers in the chloromethylation products consisted in oxidation with dilute nitric acid at 200° and quantitative separation of the resulting benzenedicarboxylic acids. These determinations indicated the formation of 77% of para isomer and 23% of ortho isomer from ethylbenzene, 87% of para isomer and 13% of ortho isomer from cumene, and 100% of para isomer from tert-

Special interest was attached to the determination of the pattern of variation of the proportions of isomers in the chloromethylation of the various halobenzenes. For the case of nitration [10] it was shown that the amount of ortho isomer formed rises gradually as we pass from fluoro- to iodo-benzene. In spite of the prevalent view concerning the diffuculty of chloromethylating halobenzenes, we developed a method for the chlorination of these compounds in good yield (75-80%). We showed that, in all cases, the reaction gives mixtures of o- and p-(chloromethyl) derivatives; the proportions of the isomers are given in Table 3.

TABLE 3

Substance being chloro-methylated	Composition of chloromethylation product (%)	
	para isomer	ortho isomer
C_6H_5F	89	11
C_6H_5Cl	63.7	36.3
C_6H_5Br	56.9	43.1
C_6H_5I	52.4	47.6

The relative amounts of isomers were determined by comparison of the results of chromium trioxide oxidation with the results of the oxidation of the pure para isomer under strictly identical conditions. In this oxidation reaction ortho derivatives of the benzene series are completely oxidized with breakdown of the benzene nucleus. For each chloromethylation product, duplicate oxidations were carried out and agreeing results were obtained for the amount of halobenzoic acid formed. In order to check the reliability of this determination, a definite amount of crystalline para isomer was frozen out of the mixture of chloromethyl derivatives and the relative amounts of isomers were determined in the residual mixture by oxidation with chromium trioxide; from the results obtained, the relative amounts of isomers in the original mixture were calculated. The verified determination of the compositions of the mixtures gave the following results: fluorobenzene gave 89.6% of para isomer, chlorobenzene gave 62.6%, bromobenzene gave 58%, and iodobenzene gave 53.0%.

The direct determination of ortho isomers was carried out by oxidation of the mixture of chloromethyl derivatives with dilute nitric acid at 200° and separation of the ortho and para isomers from the resulting mixture of halobenzoic acids. The difficulties associated with the isolation of o- and p-halobenzoic acids did not permit the compositions of the mixtures to be determined quantitatively in this way. However, in the oxidation of the chloromethyl derivatives of halobenzenes, the corresponding pure o-and p-halobenzoic acids

were isolated in all cases.

Hence, our results on the relative amounts of ortho and para isomers formed in the chloromethylation of halobenzenes are in agreement with the corresponding data for the nitration of halobenzenes and for the recently described chlorination of halobenzenes with ferric chloride [11].

We may now speak definitely of a regular change in the relative amounts of ortho and para isomers formed by substitution in the series of halobenzenes, there being a gradual reduction in the amount of para isomer and increase in the amount of ortho isomer as we pass from fluoro- to iodo-benzene. This phenomenon in the case of nitration was explained as due to change in the deactivation of the ortho position with change in the electronegativity of the halogen substituent F > Cl > Br > I [10]. This conclusion is in accord with the change in the dipole moments of halobenzenes, which indicates that the tendency to withdraw electrons from the aromatic nucleus changes in the following order: F > Cl > Br > I.

However, it is difficult to agree in this case with the idea of the "overpowering" of steric hindrance by polar factors, just as it would be strange to read of substantial steric hindrance in the nitration of toluene in the ortho position. It is known that in the latter case the ortho derivative is formed in an amount equal to more than 50% of the total yield of nitrotoluenes. It is known also that methyl is a more bulky substituent than fluorine and chlorine and is close in size to bromine and iodine [12]. It is clear that the size of the halogen substituent, even in the case of iodobenzene, cannot greatly hinder ortho substitution by a small attacking agent such as NO_2^+. It is natural to expect that steric hindrance can be a determining factor for the orientation of reaction only for a given relation between the sizes of substituent and attacking agent; until this limiting relation is reached polar factors may be dominant, particularly for substituents which have a very marked action on the nucleus.

It is interesting to compare our results on orientation in chloromethylation with analogous results on nitration – the reaction most frequently used in the study of the laws of electrophilic substitution (Table 4).

TABLE 4

Original substance	Chloromethylation (composition of mixture, %)			Nitration (composition of mixture, %)		
	para isomer	ortho isomer	meta isomer	para isomer	ortho isomer	meta isomer
$C_6H_5CH_3$	48.3	51.7	—	38	58	4
$C_6H_5CH_2COOC_2H_5$	60.4	27.0	12.6	47.4	42	10.6
$C_6H_5CH_2Cl$	69	16	15	52.5	32	15.5
$C_6H_5CH_3$	48.3	51.7	—	38	58	4
$C_6H_5CH_2CH_3$	70	30	—	45	54	—
$C_6H_5CH(CH_3)_2$	85	15	—	62	30	7.7
$C_6H_5C(CH_3)_3$	100	0	—	72.7	15.8	11.5
C_6H_5F	89	11	—	87	12	—
C_6H_5Cl	63.7	36.3	—	69	31	—
C_6H_5Br	56.9	43.1	—	59	41	—
C_6H_5I	52.4	47.6	—	59	41	—

It follows from this comparison that, with respect to the proportions of isomers formed, chloromethylation follows the same laws as nitration. It was previously established [2] that the laws determining the dependence of the rate of the chloromethylation reaction on the identity of the substituent present in the aromatic nucleus are the same as for other reactions of electrophilic substitution in the aromatic nucleus. The fact that these important laws are common to all these reactions means that we may confidently describe chloromethylation as a reaction of electrophilic substitution.

EXPERIMENTAL

Chloromethylation of Ethyl Phenylacetate

Hydrogen chloride was passed for 30 minutes into a vigorously stirred mixture of 100 ml of carbon

tetrachloride, 6 g of paraform, and 6 g of anhydrous zinc chloride. Addition was then made of 32.8 g of ethyl phenylacetate and 2 g of zinc chloride, and the reaction mixture was stirred for seven hours at 50°. The product was washed with water, with sodium bicarbonate solution, and again with water, and it was dried with calcium chloride. Fractionation gave 5.6 g of unchanged ethyl phenylacetate and 11 g (31%) of a mixture of chloromethyl derivatives of ethyl phenylacetate: b.p. 148 – 151° (8 mm); n_D^{20} 1.5240; d_4^{20} 1.1623; found MR 55.96; calculated MR 55.82

	Found %:	C 61.97; 61.79; H 6.17; 6.08
$C_{11}H_{13}O_2Cl$.	Calculated %:	C 62.11; H 6.11

The low yield of chloromethyl derivatives is to be explained by partial splitting of the ester with formation of phenylacetic acid.

Chloromethylation of Benzene

Hydrogen chloride was passed for one hour into a vigorously stirred mixture of 200 ml of carbon tetrachloride, 30 g of paraform, and 20 g of zinc chloride, and 39 g of benzene was then added dropwise. In the middle and at the end of the addition of benzene, 10-g portions of zinc chloride were added. The reaction mixture was stirred for 13 hours at 50°; the product was washed (with water, with sodium bicarbonate solution, and again with water) and was dried over calcium chloride. Solvent was distilled off, and 12 g of benzyl chloride, b.p. 60-61° (10 mm) then distilled over. When cooled, the residue partially crystallized out. Filtration gave 20.5 g of α,α'-dichloro-p-xylene; after being washed with alcohol and dried in a desiccator it melted at 99-100.5°, which is in accord with data in the literature [4]. Vacuum fractionation of the oily residue remaining after the separation of crystalline α,α'-dichloro-p-xylene gave 9.5 g of a mixture of the three α,α'-dichloroxylenes, b.p. 118.5-120° (9 mm).

	Found %:	Cl 40.52; 40.56
$C_8H_8Cl_2$.	Calculated %:	Cl 40.52

Oxidation of α,α'-Dichloro-p-xylene with Chromium Trioxide

A mixture of 5.1 g of α,α'-dichloro-p-xylene (m.p. 99-100.5°), 30 g of chromium trioxide, 90 ml of water, 90 ml of acetic acid, and 30 ml of concentrated sulfuric acid was refluxed until an exothermic reaction set in. When heat ceased to be evolved, the reaction mixture was boiled for a further 90 minutes. The mixture was cooled and filtered. The terephthalic acid so obtained was dried: it amounted to 4.76 g (98.3%). A mixture of 1 g of this acid, 15 ml of methanol, and 1.5 ml of concentrated sulfuric was refluxed for 13 hours. The usual treatment gave 1.02 g (91%) of dimethyl terephthalate, m.p. 141-142° (from methanol), undepressed by admixture of a known sample.

Hydrolysis of α,α'-Dichloro-p-xylene

A mixture of 17.5 g of α,α'-dichloro-p-xylene (m.p. 99-100.5°), 100 ml of water, and 15 g of chalk was vigorously stirred at the boil for 24 hours. The usual treatment gave 10.8 g (78.3 %) of p-xylene-α,α'-diol, m.p. 111-112° (from water) [13].

Chloromethylation of Benzyl Chloride

The chloromethylation of benzyl chloride was carried out as described for the case of benzene, with the exception that benzyl chloride was added immediately to the reaction mixture before passage of hydrogen chloride was begun. Reaction between 63.3 g of benzyl chloride, 15 g of paraform, and 20 g of anhydrous zinc chloride gave 20 g of crystalline α,α'-dichloro-p-xylene, m.p. 99-100°, and 9.7 g of a liquid mixture of the three α,α'-dichloroxylenes, b.p. 111-114° (6 mm).

Oxidation of Mixtures of Chloromethyl Derivatives with Dilute Nitric Acid at 200°

a) A mixture of 60 ml of 20 % nitric acid and 3.81 g of the above-described mixture of chloromethyl

derivatives of ethyl phenylacetate was prepared in a 200-ml rotating autoclave. The autoclave was filled with nitrogen at a pressure of 30 atm, and the reaction mixture was stirred at 200° for 90 minutes. From the cooled reaction mixture, 1.97 g of a mixture of terephthalic and isophthalic acids was filtered off. The mother liquor was evaporated down to low bulk, and recrystallization of the recipitate from 5% hydrochloric acid gave 0.73 g of phthalic acid. The total yield of acids was 90%. The mixture of terephthalic and isophthalic acids (1.97 g) was separated via their barium salts, which were prepared by treating the acids with barium oxide. The resulting mixture of barium salts was heated with a little water and left overnight. Undissolved barium terephthalate was filtered off; treatment with acid gave 1.6 g of terephthalic acid, the dimethyl ester of which melted at 141-142° and showed no depression of melting point in admixture with a known sample. Acidification of the mother liquor remaining after separation of barium terephthalate gave 0.36 g of isophthalic acid, and treatment of this with ethereal diazomethane gave 0.36 g of dimethyl isophthalate, m.p. 62-63° (from heptane), undepressed by admixture of a known sample. The 0.73 g of phthalic acid was converted into its anilide by heating it with aniline; m.p. 209-210° (from methanol), undepressed by admixture of specially prepared phthalanilide. From the oxidation results it follows that, in the chloromethylation of ethyl phenylacetate, 60.4% of para isomer, 27% of ortho isomer, and 12.6% of meta isomer are formed.

b) The oxidation of the mixture of α,α'-dichloroxylenes obtained in the chloromethylation of benzene was carried out similarly. Reaction was between 3.13 g of the above-described liquid mixture of α,α'-dichloroxylenes remaining after the separation of crystalline α,α'-dichloro-p-xylene and 60 ml of 20% nitric acid. The products were 1.51 g of a mixture of terephthalic and isophthalic acids, insoluble in the cold, and 1.49 g of phthalic acid, separated by evaporation of the mother liquor. The yield of acids was quantitative. When heated with water, the mixture of acids (1.51 g) dissolved almost completely. Undissolved terephthalic acid (only 0.1 g) gave the dimethyl ester, m.p.. 140-141°, when treated with ethereal diazomethane. Phthalic acid was identified through its anilide, m.p. 209-210°, and isophthalic acid through its dimethyl ester, m.p. 62-63°. On the basis of the amounts of acids obtained in the oxidation, and also of the amount of α,α'-dichloro-p-xylene already isolated (20 g), the relative amounts of isomeric α,α'-dichloroxylenes obtained in the chloromethylation of benzene were calculated: 69% of para isomer, 16% of ortho isomer, and 15% of meta isomer.

Chloromethylation of Ethylbenzene, Cumene, and tert-Butylbenzene in presence of Zinc Chloride

a) Hydrogen chloride was passed for 45 minutes into a mixture of 150 ml of carbon tetrachloride, 17 g of paraform, and 10 g of anhydrous zinc chloride at room temperature. The temperature of the reaction mixture rose to 40-50°. Ethylbenzene (53 g) was added dropwise to the mixture at 50°. When the addition was complete, the reaction mixture was stirred for 20 minutes, and it was then washed (with water, with sodium bicarbonate solution, and again with water) and dried over calcium chloride. Solvent and unchanged ethylbenzene (7.4 g) were distilled off, and the residue was vacuum-fractionated. The products were 34.4 g (44.5%) of a mixture of ethylbenzyl chlorides, b.p. 95-101° (12 mm) [14] and 12 g of the corresponding diarylmethane derivative, b.p. 150° (12 mm).

b) In a similar way, addition of 60 g of cumene over a period of 105 minutes to a mixture of 150 ml of carbon tetrachloride, 20 g of paraform, and 10 g of zinc chloride previously saturated with hydrogen chloride gave 37.7 g (45%) of a mixture of isopropylbenzyl chlorides, b.p. 100-110° (15 mm) [14]. The residue of diarylmethane derivative amounted to about 10 g.

c) Similarly, addition of 34 g of tert-butylbenzene over a period of three hours to a mixture of 75 ml of carbon tetrachloride, 10 g of paraform, and 5 g of zinc chloride previously saturated with hydrogen chloride gave 5.3 g (58%) of p-tert-butylbenzyl chloride, b.p. 101-105° (7 mm); 27.3 g of tert-butylbenzene was recovered unchanged, and there was a residue from the distillation of 0.9 g.

Chloromethylation of Ethylbenzene, Cumene, and tert-Butylbenzene in a Medium of Concentrated Hydrochloric Acid in absence of Zinc Chloride

a) Hydrogen chloride was passed for five hours into a vigorously stirred mixture of 90 ml of concentrated hydrochloric acid, 30 g of paraform, and 80 g of ethylbenzene. The reaction mixture was then stirred for 20 hours at 50-55°. The organic layer was washed (with water, with sodium bicarbonate solution, and again with

water) and dried over calcium chloride. Unchanged ethylbenzene (32 g) was distilled off, and vacuum distillation of the residue gave 42 g of a mixture of ethylbenzyl chlorides, b.p. 88-92° (10 mm). The yield was 60% on the amount of ethylbenzene that reacted. The residue from the distillation amounted to 2.9 g.

b) Similarly, passage of hydrogen chloride for 18 hours through a mixture containing 85 g of cumene followed by stirring at 50-55° for 27 hours gave 36 g of a mixture of isopropylbenzyl chlorides, b.p. 98-102° (11 mm). The yield was 50% on the amount of cumene that reacted (35.3 g was recovered unchanged). The residue from the distillation amounted to 4 g.

c) Passage of hydrogen chloride at 55° for 26 hours into a mixture of 67 g of tert-butylbenzene, 20 g of paraform, and 60 ml of concentrated hydrochloric acid gave 9.1 g (35%) of p-tert-butylbenzyl chloride, b.p. 101-107° (7 mm); 47.7 g of tert-butylbenzene was recovered unchanged, and the residue from the distillation amounted to 2.4 g.

Oxidation of the Chloromethylation Products from Ethylbenzene and Cumene with Chromium Trioxide

A mixture of 4.5 g of the mixture of chloromethyl derivatives of ethylbenzene, 30 g of chromium trioxide, 90 ml of water, 90 ml of acetic acid, and 30 ml of concentrated sulfuric acid was refluxed until an exothermic reaction set in. When heat was no longer evolved, the reaction mixture was boiled for a further one hour. Cooling, filtration, and drying of the residue gave 2.85 g of terephthalic acid. In a repeat experiment 2.95 g of terephthalic acid was obtained. The mean yield was 60%. Refluxing of 1.0 g of this acid with 15 ml of methanol and 1.5 ml of concentrated sulfuric acid for 11 hours gave 0.97 g (91%) of dimethyl terephthalate, m.p. 141-142°.

Comparison of these results with results on the oxidation of the mixture of chloromethyl derivatives of toluene under strictly comparable conditions shows that the chloromethylation of ethylbenzene gives a mixture of ethylbenzyl chlorides consisting of 70% of para isomer and 30% of ortho isomer.

In the oxidation of 4.91 g of a mixture of chloromethyl derivatives of cumene under analogous conditions, in the first experiment 3.54 g and in the second experiment 3.45 g of terephthalic acid was obtained; the acid was identified through its dimethyl ester. The average yield was 72.4%, which corresponds to the presence in the mixture of 85% of para isomer and 15% of ortho isomer of isopropylbenzyl chloride.

Oxidation of the Chloromethylation Products from Ethylbenzene, Cumene, and tert-Butylbenzene with Dilute Nitric Acid at 200°

a) A mixture of 75 ml of 5% nitric acid and 5.15 g of the above-described chloromethylation products from ethylbenzene was prepared in a 200-ml rotating autoclave. The reaction mixture was stirred at 200° for 90 minutes; the initial pressure of nitrogen was 40 atm. The reaction mixture was cooled, and 2.94 g of terephthalic acid was filtered off. Evaporation of the mother liquor and recrystallization from 5% hydrochloric acid gave 0.87 g of phthalic acid. The total yield of acids was 70%. Terephthalic acid was purified through its barium salt; no water-soluble barium isophthalate was detected. The purified terephthalic acid was converted into its dimethyl ester, m.p. 141-142°, by the action of ethereal diazomethane. Phthalic acid was converted into its anilide, m.p. 209-210°. The amounts of the acids isolated corresponded to 77% of para isomer and 23% of ortho isomer of ethylbenzyl chloride in the mixture obtained by the chloromethylation of ethylbenzene.

b) Oxidation of 5 g of the mixture of chloromethyl derivatives of cumene with 75 ml of 20% nitric acid at 200° for 90 minutes without any initial pressure of nitrogen gave 3.38 g of terephthalic acid and 0.5 g of phthalic acid, which was precipitated after long standing from mother liquor that had been evaporated down to low bulk. The total yield of acids was 78.8%. Refluxing of 1.0 g of terephthalic acid and 15 ml of methanol in presence of 1.5 ml of concentrated sulfuric acid gave 1.03 g (91%) of the dimethyl ester, m.p. 141-142°. Phthalic acid was converted into its anilide, m.p. 208-209°, undepressed by admixture of a known sample. By conversion of the terephthalic acid obtained into its barium salt it was shown that isophthalic acid was absent.

c) Oxidation of 5 g of the mixture of chloromethyl derivatives of tert-butylbenzene with the aid of 80 ml of 20% nitric acid at 200° for 90 minutes without initial pressure of nitrogen gave 3 g (66%) of terephthalic

acid, the dimethyl ester of which melted at 141-142°. When the mother liquor was evaporated, no phthalic acid could be detected.

Chloromethylation of Fluorobenzene

Hydrogen chloride was passed for 90 minutes into a vigorously stirred mixture of 100 ml of carbon tetrachloride, 30 g of paraform, and 20 g of anhydrous zinc chloride. Addition was then made of 48 g of fluorobenzene (b.p. 84-85°), and stirring was continued for 5.5 hours at 50°. A further 5 g of zinc chloride was added 90 minutes before stirring was discontinued. The reaction mixture was set aside overnight. It was then washed (with water, with sodium bicarbonate solution, and again with water) and dried over calcium chloride. Fractionation gave 56.2 g (78%) of a mixture of fluorobenzyl chlorides, b.p. 69-74° (17 mm), from which 20% of low-melting crystalline para isomer [6] was isolated by chilling. Distillation of the residue (5.5 g) gave 3.35 g of a substance of b.p. 125-135° (14 mm), which was clearly the diarylmethane derivative.

Oxidation of the Chloromethylation Product from Fluorobenzene with Chromium Trioxide

A mixture of 2 g of p-fluorobenzyl chloride, 8.0 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 8 ml of concentrated sulfuric acid was refluxed for two hours. Cooling, filtering, and drying of the residue gave 1.54 g (79.8%) of p-fluorobenzoic acid, m.p. 184-185.5°, undepressed by admixture of p-fluorobenzoic acid prepared by the oxidation of 4'-fluoroacetophenone. In a repeat experiment 1.53 g of p-fluorobenzoic acid was obtained.

Oxidation under strictly identical conditions of 2 g of a mixture of chloromethylation products from fluorobenzene from which para isomer had not been separated gave 1.37 g (71%) of p-fluorobenzoic acid, m.p. 184-185°. In a repeat experiment 1.36 g of p-fluorobenzoic acid was obtained. The oxidation results show that the mixture of fluorobenzyl chlorides obtained in the chloromethylation of fluorobenzene contains 89% of para isomer and 11% of ortho isomer.

Oxidation under the same conditions of 2 g of the above-described mixture of chloromethylation products from fluorobenzene from which 20% of para isomer had been frozen out gave 1.35 g (70%) of p-fluorobenzoic acid. In a repeat experiment 1.35 g of p-fluorobenzoic acid was again obtained. It follows from these results that the original mixture of fluorobenzyl chlorides contained 89.6% of para isomer.

Chloromethylation of Chlorobenzene

Hydrogen chloride was passed for 75 minutes into a vigorously stirred mixture of 200 ml of carbon tetrachloride, 30 g of paraform and 50 g of anhydrous zinc chloride. Addition was then made of 112 g of chlorobenzene at 50°, and stirring at this temperature was continued for five hours. A further 10 g of zinc chloride was added one hour before stirring was discontinued. The reaction mixture was set aside overnight; it was then washed (with water, with sodium bicarbonate solution, and again with water) and dried over calcium chloride. Fractionation gave 27.4 g of unchanged chlorobenzene and 75.5 g (62%) of its chloromethylation product, b.p. 113-116° (34 mm), from which, by chilling, 30% of crystalline p-chlorobenzyl chloride, m.p. 27-28° [4], was isolated. The residue from the distillation amounted to 8.3 g.

Oxidation of the Chloromethylation Product from Chlorobenzene with Chromium Trioxide

A mixture of 2 g of crystalline p-chlorobenzyl chloride, m.p. 27-28°, 8.6 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 8.6 ml of sulfuric acid was refluxed for two hours. Cooling, filtering, and drying of the residue gave 1.68 g (87%) of p-chlorobenzoic acid, m.p. 241-243°, undepressed by admixture of a known sample. In a repeat experiment, 1.67 g of p-chlorobenzoic acid was obtained.

Oxidation under strictly identical conditions of 2 g of the mixture of chloromethylation products from chlorobenzene gave 1.06 g (55.4%) of p-chlorobenzoic acid, m.p. 241-242°. In a repeat experiment 1.07 g of p-chlorobenzoic acid was obtained. The oxidation results show that the mixture of chlorobenzyl chlorides contained 63.7% of para isomer and 36.3% of ortho isomer. In the oxidation under the same conditions of 2 g of the mixture of chlorobenzyl chlorides remaining after crystalline para isomer had been frozen out, 0.79 g

(40.9%) of p-chlorobenzoic acid was obtained. In a repeat experiment 0.79 g of p-chlorobenzoic acid was obtained. Calculation shows that the original mixture of chlorobenzyl chlorides contained 62.6% para isomer.

Chloromethylation of Bromobenzene

Hydrogen chloride was passed for one hour into a vigorously stirred mixture of 200 ml of carbon tetrachloride, 30 g of paraform, and 40 g of anhydrous zinc chloride. Addition was then made of 157 g of bromobenzene, and stirring was continued for five hours at 50°. A further 10 g of zinc chloride was added one hour before stirring was discontinued. The reaction mixture was set aside overnight; it was then washed (with water, with sodium bicarbonate solution, and again with water) and dried over calcium chloride. Fractionation gave 61.9 g of unchanged bromobenzene and 95 g (76.2%) of the chloromethylation product of bromobenzene, b.p. 83-87° (3 mm), from which, by chilling, 35% of crystalline p-bromobenzyl chloride, m.p. 37-38° (4 mm) [4], was isolated. The residue from the distillation amounted to 7.5 g.

Oxidation of the Chloromethylation Product from Bromobenzene with Chromium Trioxide

A mixture of 2 g of crystalline p-bromobenzyl chloride, m.p. 37-38°, 11.0 g of chromium trioxide, 40 ml of water, 40 ml of acetic acid, and 11 ml of concentrated sulfuric acid was refluxed for two hours. Cooling, filtering, and drying of the residue gave 1.72 g (88.2%) of p-bromobenzoic acid, m.p. 251-253°, undepressed by admixture of a known sample. In a repeat experiment 1.71 g of p-bromobenzoic acid was obtained.

Oxidation under identical conditions of 2 g of the mixture of chloromethylation products from bromobenzene gave 0.98 g (50.2%) of p-bromobenzoic acid, m.p. 251-263°. In a repeat experiment 0.98 g of p-bromobenzoic acid was again obtained. The oxidation results show that the mixture of bromobenzyl chlorides contained 56.9% of para isomer and 43.1% of ortho isomer. In the oxidation under the same conditions of 2 g of the mixture of bromobenzyl chlorides remaining after crystalline para isomer had been frozen out, 0.62 g of p-bromobenzoic acid was obtained. In a repeat experiment 0.67 g of p-bromobenzoic acid was obtained. The average yield was 33.3%. Calculation shows that the original mixture of bromobenzyl chlorides contained 58% of para isomer.

Chloromethylation of Iodobenzene

Hydrogen chloride was passed for 50 minutes into a vigorously stirred mixture of 200 ml of carbon tetrachloride, 23 g of paraform, and 30 g of anhydrous zinc chloride. Addition was then made of 152 g of iodobenzene, and the reaction mixture was stirred at 50° for five hours. A further 7.5 g of zinc chloride was added one hour before stirring was discontinued. The reaction mixture was set aside overnight. It was washed (with water, with sodium bicarbonate solution, and again with water) and dried over calcium chloride. Fractionation gave 81.8 g of unchanged iodobenzene and 77 g (76%) of the chloromethylation product from iodobenzene, b.p. 113-117° (5 mm), from which about 30% of crystalline p-iodobenzyl chloride, m.p. 52-53°, was frozen out; this substance has been previously described as a liquid [15]. The residue from the distillation amounted to 7.2 g.

Oxidation of the Chloromethylation Product from Iodobenzene with Chromium Trioxide

A mixture of 2 g of crystalline p-iodobenzyl chloride, m.p. 52-53°, 5 g of chromium trioxide, 25 ml of water, 25 ml of acetic acid, and 5 ml of concentrated sulfuric acid was refluxed for one hour. Cooling, filtering, and drying of the residue gave 1.54 g of p-iodobenzoic acid, m.p. 270-272°, undepressed by admixture of a known sample. In a repeat experiment 1.63 g of p-iodobenzoic acid was obtained. The average yield was 1.6 g (81.6%).

Oxidation under identical conditions of 2 g of the mixture of iodobenzyl chlorides obtained in the chloromethylation of iodobenzene gave 0.86 g of p-iodobenzoic acid, m.p. 270-272°. In a repeat experiment 0.82 g of p-iodobenzoic acid was obtained. The average yield was 0.84 g (42.8%). The oxidation results show that the mixture of iodobenzyl chlorides contained 52.4% of para isomer and 47.6% of ortho isomer. In the oxidation under the same conditions of 2 g of the mixture of iodobenzyl chlorides remaining after crystalline para isomer had been frozen out, 0.54 g of p-iodobenzoic acid was obtained. In a repeat experiment

0.56 g of p-iodobenzoic acid was obtained. The average yield was 0.55 g (28.0%). Calculation shows that the mixture of iodobenzyl chlorides contained 53% of para isomer.

Oxidation of the Chloromethylation Products from Halobenzenes with Dilute Nitric Acid at 200°

a) A mixture of 80 ml of 20% nitric acid and 5 g of the mixture of fluorobenzyl chlorides was prepared in a 200-ml rotating autoclave. The mixture was stirred at 200° for 90 minutes. The reaction mixture was cooled, and filtration then gave 4.29 g of p-fluorobenzoic acid. After crystallization from water it had m.p. 182-183.5°, undepressed by admixture of a known sample. After evaporation to small bulk, the mother liquor gave 0.22 g of o-fluorobenzoic acid, m.p. 118-120° after two recrystallizations from water. The total yield of acids was 93.1%.

b) Similarly, from 5.0 g of the mixture of chlorobenzyl chlorides, in all (including material obtained by evaporation of the mother liquor) 4.11 g (84.5%) of a mixture of chlorobenzoic acids was obtained, and this was separated through the calcium salts into pure ortho and para isomers. The mixture of acids was dissolved in aqueous ammonia and, after being filtered, the solution was boiled until free of excess of ammonia (judged by odor). A solution of pure calcium chloride was added to the solution of ammonium salts. The soluble calcium p-chlorobenzoate then separated out; it was filtered off and converted into the acid by treatment with dilute hydrochloric acid. The p-chlorobenzoic acid isolated in this way had m.p. 238-240°, undepressed by admixture of a known sample. After being evaporated to small bulk the mother liquor gave the calcium salt of the ortho isomer, which was washed carefully with alcohol and converted into o-chlorobenzoic acid, m.p. 137-138°, by treatment with acid.

c) Oxidation under similar conditions of 5 g of the mixture of bromobenzyl chlorides gave 2.81 g (including 0.27 g from the mother liquor) of a mixture of bromobenzoic acids. The total yield of acids was 57.5%. Two recrystallizations of the main mixture of acids (2.54 g) gave 1 g of p-bromobenzoic acid, m.p. 248-250°, undepressed by admixture of a known sample. The 0.27 g of acids isolated from the mother liquor was purified via the silver salt, and o-bromobenzoic acid, m.p. 143-145°, was isolated by repeated crystallization from water.

Oxidation under similar conditions of the chloromethylation product from iodobenzene did not give satisfactory results, evidently owing to the occurrence of oxidation in the aromatic nucleus.

SUMMARY

1. Structural analysis by the oxidation method was carried out on chloromethylation products from ethyl phenylacetate, benzyl chloride, ethylbenzene, cumene, tert-butylbenzene, and all four monohalobenzenes. In all cases, apart from that of tert-butylbenzene, it was found that mixtures of ortho and para isomers were formed. The relative amounts of the isomers were determined and were found to depend greatly on the character of the substituent.

2. In the chloromethylation of toluene, ethylbenzene, cumene, and tert-butylbenzene, the content of para isomer in the mixture progressively increases; this is to be explained by the effect of the size of the substituent (steric factor). In the chloromethylation of halobenzenes, the amount of para isomer progressively diminishes as we pass from fluorobenzene to iodobenzene, this being determined by the ionizing effects of the halogen atoms.

3. On the basis of our results and data in the literature on reaction rates, it is concluded that chloromethylation is an electrophilic-substitution reaction.

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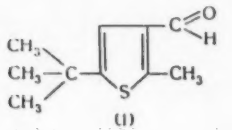
* Russian translation.

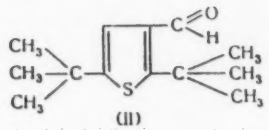
STRUCTURE OF THE ACETYLATION AND FORMYLATION PRODUCTS OF 2-tert-BUTYL-5-METHYLTHIOPHENE AND 2,5-DI-tert-BUTYLTHIOPHENE

Ya. L. Goldfarb and P. A. Konstantinov

In a previous communication [1], which was concerned with the preparation of aliphatic alcohols by the hydrogenolysis of thiophene derivatives, we described two aldehydes, which according to the course of their synthesis could be assigned the structures of 5-tert-butyl-2-methyl-3-thiophenecarboxaldehyde (I) and 2,5-di-tert-butyl-3-thiophenecarboxaldehyde (II).



(I)



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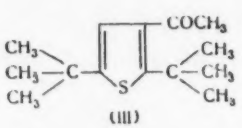
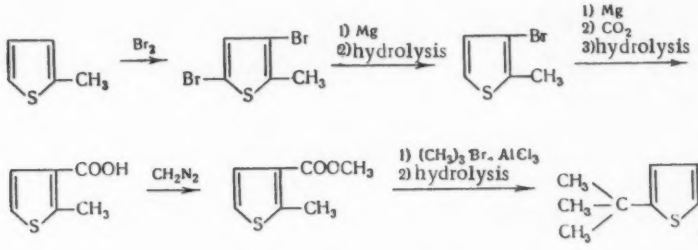


(III)

However, two considerations made this view not altogether well founded: 1) the entry of the formyl group into the β-position next to the methyl group is not the only possible direction in which formylation under the conditions of Weston and Michaels [2] could proceed; 2) it is necessary to take account of the possibility of isomerization due to migration of a tert-butyl group. In this connection we must point out that migration of the tert-butyl group proceeds particularly readily [3] in the preparation of aromatic ketones by the Friedel-Crafts reaction. Similar isomerization might occur also in the acetylation of 2,5-di-tert-butylthiophene in presence of stannic chloride. For this reason it was necessary to confirm the structure of the ketone which Goldfarb and Korsakova [4] regarded as 2,5-di-tert-butyl-3-thienyl methyl ketone (III). We therefore undertook a study of the structures of the aldehydes (I) and (II) and of the ketone (III). The structure of the aldehyde (I) was confirmed by its oxidation to the corresponding acid, which was compared with 5-tert-butyl-2-methyl-3- thiophenecarboxylic acid (IV) prepared as follows: *

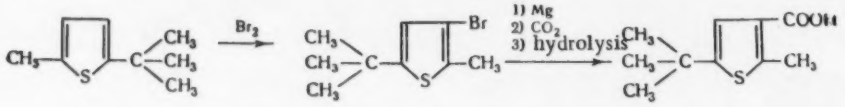


It was not clear beforehand whether it would be possible to effect the final stage – alkylation of the 2-methyl-3-thiophenecarboxylic ester to the ester of the acid (IV) – for only isolated cases of Friedel-Craft alkylation of thiophene derivatives carrying negative functions have been described in the literature [6].

* 2-Methyl-3-thiophenecarboxylic acid was prepared by the method described by Steinkopf and Jacob [5].

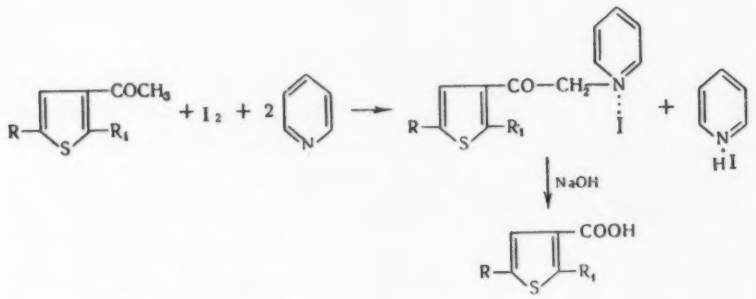
However, we were able to realize this stage without difficulty.

The product of the oxidation of the aldehyde (I) was found to be identical with the acid synthesized in accordance with the above scheme. We synthesized the same acid (IV) by the Grignard reaction from the monobromo derivative of 2-tert-butyl-5-methylthiophene. In this way the correctness of the proposed structure for the aldehyde (I) was again confirmed and the structure of the above bromo derivative was established as 3-bromo-5-tert-butyl-2-methylthiophene:



Out results are in accord with the observations of various authors, in particular Schlatter [7] and Kulka [8], on the blocking effect of the tert-butyl group. Both in formylation and in bromination, substitution occurs in the β-position next to the methyl group and not in the position next to the bulky tert-butyl group. These same results served as a starting point also for the determination of the structure of the ketone obtained by the acetylation of 2-tert-butyl-5-methylthiophene. The problem consisted in the oxidation of this ketone to the acid (IV). The first attempt – oxidation with sodium hypochlorite by Hartough and Conley's method [9] – was unsuccessful. * On the other hand, the method proposed by King [10], consisting in the simultaneous action of iodine and pyridine and subsequent splitting of the resulting pyridinium salt with alkali, enabled us to obtain the required acid in an acceptable yield.

The reaction may be indicated diagrammatically as follows:



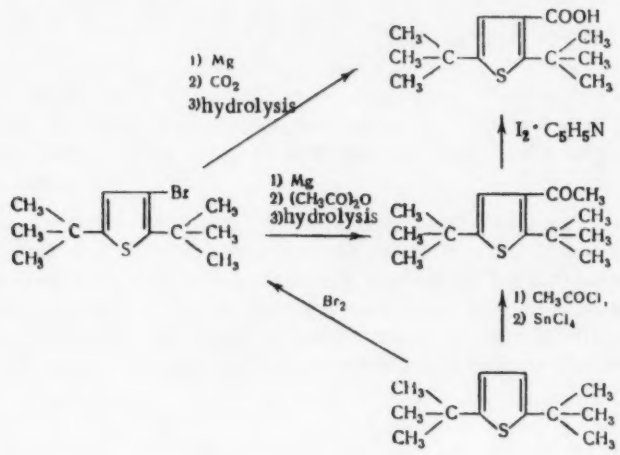
in which R and R_1 are hydrocarbon radicals.

This very interesting method enabled us to prepare also 2,5-di-tert-butyl-3-thiophenecarboxylic acid, which, as indicated in Hartough and Conley's paper [9], cannot be prepared by oxidation of the corresponding ketone with sodium hypochlorite. The lack of success of Hartough and Conley might be ascribed to the steric effect of the tert-butyl group. However, the fact that 2,5-di-tert-butyl-3-thiophenecarboxylic acid (V) is formed by the splitting of the corresponding pyridinium salt with alkali suggests that criteria of this kind must be applied with caution. This method can be used also for the preparation of other acids of the thiophene series. Thus, 2,5-dimethyl-3-thiophenecarboxylic acid (VI) was prepared by us in almost theoretical yield, whereas by the hypohalite-oxidation method we could not obtain it in yields exceeding 60 %. King's method, which is apparently the only method for the conversion of screened ketones into the corresponding acids, can be used with success for the preparation of various acids of the thiophene series.

Returning to the question of the structure of the ketone (III), we must note again (see above) that it was necessary to determine whether isomerization occurred in the preparation of the ketone owing to the presence of stannic chloride in the reaction mixture. This question was resolved as follows. By bromination of 2,5-di-tert- butylthiophene, 3-bromo-2,5-di-tert-butylthiophene was prepared. By Newman and Booth's method [11] –

* The cause of the stability of the ketone toward hypochlorite is not clear to us at present.

from this bromo compound through the organomagnesium compound, which was treated with acetic anhydride (i.e., without participation of stannic chloride) a ketone was obtained which was found to be identical with that obtained by Goldfarb and Korsakova [4]. From the same monobromo derivative we synthesized an acid with the aid of the Grignard reaction; it was found to be identical in all its properties with the acid obtained from the acetylation product of 2,5-di-tert-butylthiophene via the pyridinium salt. The results of this part of our work are illustrated in the following scheme:



EXPERIMENTAL

5-tert-Butyl-2-methyl- and 2,5-di-tert-butyl-3-thiophenecarboxaldehydes were prepared by the method described previously [1]. 2,5-Dimethyl-3-thienyl methyl ketone, 5-tert-butyl-2-methyl-3-thienyl methyl ketone, and 2,5-di-tert-butyl-3-thienyl methyl ketone were prepared by Stadnikov and Goldfarb's method — acetylation of 2,5-dimethyl-, 2-tert-butyl-5-methyl-, and 2,5-di-tert-butyl-thiophenes in presence of stannic chloride. 5-tert-Butyl-2-methyl-3-thienyl methyl ketone, previously described by Goldfarb and Korsakova [13] as a liquid, was found to be a solid, m.p. 23-24°.

5-tert-Butyl-2-methyl-3-thiophenecarboxylic Acid. A mixture of a solution of 5 g (0.026 mole) of 5-tert-butyl-2-methyl-3-thienyl methyl ketone in 15 ml of pyridine and 8.5 g (0.052 mole) of iodine was prepared in a round-bottomed flask fitted with mechanical stirrer and reflux condenser protected with a calcium chloride tube. The dark-brown solution was heated for 30 minutes in a water bath and was then set aside overnight. Excess of pyridine was distilled from the precipitate that had formed. The resulting mixture of pyridinium salts was refluxed for one hour with 200 ml of 50% aqueous ethanol containing 4 g of sodium hydroxide. The solution was cooled, diluted with an equal volume of water, and extracted with ether. The aqueous layer was separated and acidified to Congo red with 10% hydrochloric acid. The precipitated acid was filtered off, washed with ice water, and dried. The yield of acid, m.p. 128-130°, was 3 g (60%). After recrystallization from 30% aqueous alcohol and heptane the melting point was 131-132°.

	Found %:	C 60.59;	60.60;	H 7.11;	7.14;	S 15.94; 16.20
$C_{10}H_{14}O_2S$.	Calculated %:	C 60.59;		H 7.11;		S 16.17

Neutralization equivalent: Found 197.6, calculated 198.27.

3-Bromo-5-tert-butyl-2-methylthiophene. A solution of 7.7 g (0.05 mole) of 2-tert-butyl-5-methylthiophene in 100 ml of carbon disulfide was introduced into a flask fitted with dropping funnel and reflux condenser protected with a calcium chloride tube, and was boiled in a water bath for one hour while 8 g (0.05 mole) of bromine was added dropwise. Boiling then continued for a further three hours. The mixture was poured into 100 ml of cold water, and was then washed with bicarbonate solution and with water. The solution was dried with calcium chloride, solvent was distilled off, and vacuum distillation of the

residue at 17 mm gave

Fraction I, b.p. 110-113°; 0.3 g
Fraction II, b.p. 114-116°; 10 g; n_D^{20} 1.5360
Residue, 0.6 g

Refractionation gave 9 g of a product having b.p. 109-110° (16 mm); n_D^{20} 1.5361; d_4^{20} 1.3004; found MR 55.92; calculated MR 55.65*

Found %: C 46.43; 46.44; H 5.74; 5.81

$C_9H_{13}Br$. Calculated %: C 46.37; H 5.62

5-tert-Butyl-2-methyl-3-thiophenecarboxylic Acid from 3-Bromo-5-tert-butyl-2-methylthiophene. A Grignard reagent was prepared from 4 g (0.03 mole) of 3-bromo-5-tert-butyl-2-methylthiophene, 9.3 g (0.09 mole) of ethyl bromide in 60 ml of dry ether, and 3.84 g (0.14 mole) of magnesium turnings.

When spontaneous boiling ceased, the mixture was boiled and stirred for eight hours and was then transferred to a vessel containing solid carbon dioxide. The reaction product was hydrolyzed with 10% sulfuric acid, and the ether layer was separated and washed with water and with excess of 10% sodium hydroxide solution. Subsequent acidification of the aqueous solution to Congo red gave 2.1 g (62%) of the free acid, m.p. 127-128.5°; after recrystallization from alcohol and heptane it melted at 131-132° and showed no depression of melting point in admixture with the acid obtained by splitting the corresponding pyridinium salt (see above).

Oxidation of 4-tert-Butyl-2-methyl-3-thiophenecarboxaldehyde with Silver Oxide. Silver nitrate (4.3 g, i.e. 0.25 mole**) and 10ml of ethanol were added to 1.8 g (0.01 mole) of 4-tert-butyl-2-methyl-3-thiophenecarboxaldehyde in 10 ml of water. The mixture was stirred for two hours while 70 ml of 0.5 N alcoholic caustic alkali was added in equal portions. The mixture was left to the next day, when the precipitated silver was filtered off. The filtrate was saturated with carbon dioxide, and alcohol was distilled off. The residue in the flask was cooled to room temperature and extracted with ether. The aqueous layer was separated and acidified with 10% sulfuric acid. The precipitated acid was filtered off, washed with water, and dried over phosphoric oxide. The acid (1.3 g) melted at 118-124°. After recrystallization from aqueous alcohol and heptane it melted at 130.5-132° and showed no melting point depression in admixture with the acid obtained by the oxidation of 5-tert-butyl-2-methyl-3-thienyl methyl ketone with iodine and pyridine.

Condensation of Methyl 2-Methyl-3-thiophenecarboxylate with tert-Butyl Bromide. A mixture of 1 g (0.0064 mole) of methyl 2-methyl-3-thiophenecarboxylate, 0.97 g (0.007 mole) of tert-butyl bromide, and 13 ml of carbon disulfide was prepared in the three-necked flask fitted with stirrer, thermometer, and calcium chloride tube. The mixture was cooled to 0° and was stirred while 1.45 g (0.0014 mole) of anhydrous aluminum chloride was added over a period of one hour; stirring was continued further for one hour at room temperature. On the next day the reaction mixture was poured into a beaker containing 50 g of ice and 25 g of water. The aqueous layer was separated from the organic layer and was extracted with 50 ml of ether. The ether extract was added to the carbon disulfide layer, and the resulting solution was washed with bicarbonate solution and with water; it was then dried over magnesium sulfate. Solvent was distilled off, and the residue in the flask (methyl 5-tert-butyl-2-methyl-3-thiophenecarboxylate) was hydrolyzed to 5-tert-butyl-2-methyl-3-thiophenecarboxylic acid by boiling it for 6-7 hours with 30 ml of 15% potassium hydroxide. The cooled solution was washed with 20 ml of ether and acidified. The precipitated acid was filtered off and washed with ice water. The yield of crude acid, m.p. 126-128°, was 1 g (80% on the amount of methyl 2-methyl-3-thiophenecarboxylate taken).

After recrystallization from 80% aqueous alcohol the acid had m.p. 131-132°, undepressed by admixture of the acid prepared from 5-tert-butyl-2-methyl-3-thienyl methyl ketone via the pyridinium salt.

Found %: C 60.80; 60.78; H 7.21; 7.09

$C_{10}H_{14}O_2S$. Calculated %: C 60.59; H 7.11

* The atomic refraction of sulfur was taken to be 7.260.
** As in Original. Presumably 0.025 mole is intended – Publisher's note.

2,5-Di-tert-butyl-3-thiophenecarboxylic Acid. This was prepared by King's method (see above) from 2,5-di-tert-butyl-3-thienyl methyl ketone. In this case, after the intermediate product had been split with alkali, the cooled solution was acidified with 5% sulfuric acid and the desired acid separated immediately. From 23.8 g of 2,5-di-tert-butyl-3-thienyl methyl ketone we obtained 12.6 g (50%) of acid, m.p. 161-164°. After three recrystallizations from aqueous alcohol it melted at 168-169°.

	Found %:	C 64.79;	64.70;	H 8.35;	8.47;	S 12.97; 12.91
$C_{13}H_{20}O_2S$.	Calculated %:	C 64.93;		H 8.40;		S 13.33

Neutralization equivalent: found 233, calculated 230.35

Preparation of 2,5-Di-tert-butyl-3-thiophenecarboxylic Acid by the Grignard Reaction. A Grignard reagent was prepared from 3 g (0.011 mole) of 3-bromo-2,5-di-tert-butylthiophene, 1.6 g (0.011 mole) of ethyl bromide, 10 ml of dry ether, and 0.52 g (0.022 mole) of magnesium. After addition of the magnesium the mixture was boiled for 2.5 hours and was then gradually added to solid carbon dioxide. After the hydrolysis with dilute sulfuric acid, the ether layer was washed with water and dried over magnesium sulfate. Ether was distilled off and 2.7 g of crude acid was obtained. The acid was reprecipitated and then recrystallized from aqueous alcohol. The pure product (1.5 g) had m.p. 167.5-168.5°, undepressed by admixture of 2,5-di-tert-butyl-3-thiophenecarboxylic acid prepared by King's method.

2,5-Di-tert-butyl-3-thienyl Methyl Ketone. A grignard reagent prepared by the above-described procedure from 6 g (0.022 mole) of 3-bromo-2, 5-di-tert-butylthiophene was added dropwise over one hour to a stirred solution of 10 g (0.1 mole) of acetic anhydride in 250 ml of dry ether cooled to − 70°. A white precipitate formed. Stirring was continued for two hours. The cooling bath was then removed, and when the reaction mixture had attained room temperature 10 ml of 10% ammonium chloride solution was added. The ether layer was separated and washed several times with 10% caustic alkali and with water. It was dried over magnesium sulfate, and solvent was distilled off. Vacuum distillation (12 mm) of the residue gave:

Fraction I, b.p. 90-141°; 1.7 g
Fraction II, b.p. 141-144°; 1.61 g
Residue 0.28 g

Fraction II quickly solidified, and after recrystallization from alcohol and heptane it had m.p. 76-77°, undepressed by admixture of the ketone obtained by the condensation of 2,5-di-tert-butylthiophene with acetyl chloride in presence of stannic chloride.

2,5-Dimethyl-3-thiophenecarboxylic Acid. This was prepared by the oxidation of 2,5-dimethyl- 3-thienyl methyl ketone, 10 g of acid, m.p. 109-112°, was obtained. After two recrystallizations from 10% alcohol the melting point was 115-116°, and the melting point could not be raised further by further recrystallizations. For this acid the literature [14] gives m.p. 119-120°.

SUMMARY

1. It was shown that, in the formylation, acetylation, and bromination of 2-tert-butyl-5-methylthiophene, the new substituent enters the 4-position (the β-position next to the methyl).

2. It was shown that, in the acetylation of 2,5-di-tert-butylthiophene in presence of stannic chloride, no migration of the tert-butyl group occurs.

3. It was shown that it is possible to prepare thiophenecarboxylic acids containing α-alkyl radicals (methyl, tert-butyl) by the simultaneous action of iodine and pyridine on the corresponding ketone and subsequent splitting of the resulting pyridinium salt with alkali.

4. The following were prepared for the first time: 5-tert-butyl-2-methyl-3-thiophenecarboxylic acid, 2,5-di-tert-butyl-3-thiophenecarboxylic acid, and 3-bromo-5-tert-butyl-2-methylthiophene.

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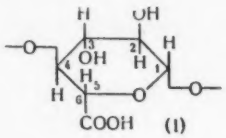
BRIEF COMMUNICATIONS

ION EXCHANGE ON DICARBOXYCELLULOSE

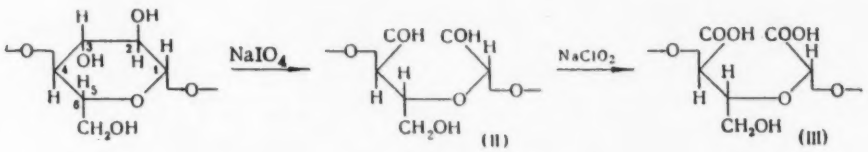
V. I. Ivanov, N. Ya. Lenshina, and V. S. Ivanova

We carried out an investigation [1] of the exchange properties of an oxidized cellulose containing units of structure (I):



(I)

There are no reports in the literature on the ion-exchange properties of the oxycellulose (III), prepared as follows:



In the present communication we examine the exchange reactions of an oxycellulose having monomer units of structure (III).

According to some investigators [2], determination of the carboxyl content of the oxycellulose (III) by the calcium acetate method gives considerably lower results than those obtained by the o-nitrophenoxide method. Taking into account recent results [3] on the difference in the rates of oxidation of 2-, 3-, and 6-aldehyde groups to carboxy groups, we attribute the high value of the carboxyl content of oxycellulose (III) to incomplete oxidation of aldehyde groups, which reduce the silver of the o-nitrophenoxide and so cause an apparent increase in the number of COOH groups.

We determined the carboxyl contents of oxycellulose (III) prepared by our modified procedure by two methods, and the results are given in Table 1.

It will be seen from Table 1 that the two methods are in close agreement. We find confirmation of these results in the work of Davidson [4].

EXPERIMENTAL

We investigated the ion-exchange properties of the oxycellulose (III) by the method described previously [1]. The initial solutions selected were nickel chloride (0.005 M, pH about 6), ferric chloride (0.005 M, pH about 2), and nickel acetate (0.005 M, pH about 7).

TABLE 1

Comparative Data on the Determination of Carboxy Groups by Two Methods in Cellulose Oxidized by Sodium Periodate and Sodium Chlorite

Sample No.	COOH content by Ca acetate method (%)	COOH content by o-nitrophenoxide method (%)
1	11.9 12.0	11.8 11.9
2	1.7 1.6	1.7 1.8

TABLE 2

Absorption of Ni^{2+} and Fe^{3+} by Oxycellulose (III), and their Desorption

Sample No.	COOH content (mg-equiv/g)	Ni^{2+} (meq/g)		Fe^{3+} (meq/g)	
		absorption	desorption	absorption	desorption
1	1	0.9	0.8	1.1	0.8
2	1.2	1.1	0.9	1.4	1.2
3	2.0	2.2	2.0	2.2	2.0
4	2.8	3.2	3.0	—	—

The experimental results on the absorption of Ni^{2+} and Fe^{3+} are given in Table 2.

It follows from Table 2 that the amounts of Ni^{2+} and Fe^{3+} absorbed are identical with the amounts desorbed. For the desorption of Ni^{2+} 0.01-0.1 N HCl was used, but for the desorption of Fe^{3+} 5 N HCl was required. This behavior of cellulose salts toward acids makes it possible to use such preparations for the selective separation of a mixture of cations.

The fact that the amounts of Ni^{2+} and Fe^{3+} absorbed by oxidized celluloses are equivalent enables us to conclude that inorganic cations interact mainly with the carboxyls of the cellulose. The absorption of Ni^{2+} by oxycellulose (III) from a solution of acetates is somewhat different from the absorption of Ni^{2+} by oxycellulose (I) from the same solution. The results are given in Table 3.

TABLE 3

Comparative Data on the Absorption of Ni^{2+} (mg-equiv per gram of absolutely dry material) by Oxycelluloses (III) and (I) having COOH Contents of 2.7 mg-equiv/g from Sodium Acetate Solution

Filtrate No.	Oxycellulose (III)		Oxycellulose (I)	
	Absorption of Ni^{2+} (mg-equiv/g)	Presence of nickel in filtrate	Absorption of Ni^{2+} (mg-equiv/g	Presence of nickel in filtrate
1—10	1.410	Absent	1.410	Absent
11	0.141	"	0.015	Present
12	0.141	"	0.015	"
13	0.141	"	0.020	"
14	0.141	"	0.010	"
15	0.040	Present	0.010	"
1—15	2.014		1.480	

It will be seen from Table 3 that in the case of oxycellulose (III) Ni^{2+} makes its appearance in the 15th filtrate, whereas it appears in the 11th filtrate in the case of oxycellulose (I), so that in the first case the dynamic exchange capacity is 0.74 of the total exchange capacity, and in the second case it is 0.5. On the basis of these results, it must be supposed that the chelating positions of the carboxyls at C-2 and C-3 in the oxycellulose molecule confer special absorption properties, the detailed study of which would be of interest.

SUMMARY

1. It was shown that, under given conditions, the extent to which nickel and ferric cations are sorbed by cellulose oxidized with sodium periodate and sodium chlorite is equivalent to the carboxyl content.

2. It was shown that, in the case of nickel acetate, the dynamic exchange capacities of oxycelluloses (I) and (III) are 0.5 and 0.74, respectively, of the total exchange capacity.

3. It was suggested that the peculiar features of the absorption of ions by oxycellulose (III) must be attributed to the chelating positions of the carboxy groups in the glucose unit.

4. The variation of the strength of the bond between oxycellulose (III) and metal ion was demonstrated with nickel and ferric ions as examples. This variation can be applied in the separation of cations.

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CHEMICAL CHANGES PRODUCED IN CELLULOSE BY ACTIVATED OXIDATION WITH HYPOCHLORITE

E. D. Kaverzneva, V. I. Ivanov, and G. A. Krylova

The oxidation of cellulose can be considerably accelerated by the introduction of activators into the oxidizing solution [1]. The oxidation of cellulose by hypochlorite activated by substances such as ammonia, ammonium chloride, and urea was studied by Zakoshchikov [2], who established the pH limits within which reaction proceeded, and advanced some hypotheses concerning the mechanism of activated oxidation. We were interested in determining the effect of the activation process on the chemical changes produced in cellulose by hypochlorite.

EXPERIMENTAL

In order to elucidate this question, we investigated the chemical changes undergone by sulfate wood cellulose in ordinary and activated oxidation by hypochlorite. We used urea as activator, because preliminary experiments showed that it had some advantages with respect to the properties of the resulting oxycellulose. Experiments were carried out on purified cellulose and on a preparation taken directly after boiling and chlorination.

TABLE 1

Oxidation conditions	Degree of oxidation (mg-equiv per 100 glucose residues)	Total COOH groups (%)
30 minutes with activation	1.35	0.16
30 minutes without activation	1.06	0.07

The oxidation was carried out under the following conditions: 1) ordinary oxidation - 0.1 N NaOCl, pH 11, 20°, 1-24 hours, liquor ratio 20 : 1; 2) activated oxidation – 0.1 N NaOCl, pH 11, 20°, 5-60 minutes, 0.025 mole of urea per mole of NaOCl, liquor ratio 20 : 1. The resulting preparations were washed carefully, and analysis was made for total and uronic carboxyls and total carbonyl and aldehyde groups; the degree of polymerization was determined from the viscosity in 0.1% solution, and the whiteness was determined by previously described methods [3]. The considerable acceleration produced by activation in the oxidative process will be seen from Table 1.

It was convenient to compare the chemical changes for preparations of identical degree of oxidation, as a measure of which we took the sum of the amounts of carboxyls and carbonyls formed, expressed in equivalents per 100 glucose residues. In Table 2 we compare the analytical results on four preparations obtained by activated oxidation (in one stage of 30 minutes, or in two stages of 30 minutes each) with the mean values for preparations oxidized to the same extent with hypochlorite in absence of activator (1.35 and 2.26 equivalents of functional groups, respectively, per 100 glucose residues). Aldehyde groups are not given in Table 2, for they were present in very small amount and this amount did not increase with increase in the extent of oxidation.

The quantitative proportions of functional groups in the preparations obtained by ordinary and activated oxidation are very close, which indicates the similarity of the oxidation processes in the two cases.

In spite of the close similarity between the oxidized celluloses with respect to the nature of the functional

TABLE 2

Oxidation conditions	Content of functional groups (%)			Total CO / Total COOH
	Total COOH	Uronic COOH	Total CO	
Purified Cellulose				
30 minutes with activation	0.16	0.15	0.15	0.94
Ditto	0.16	0.09	0.12	0.75
3.5 hours without activation	0.17	0.13	0.13	0.76
Unpurified cellulose				
30 minutes + 30 minutes with activation	0.26	—	0.25	0.96
Ditto	0.26	—	0.21	0.81
3 hours without activation	0.30	0.17	0.19	0.63

groups, the products of ordinary and activated oxidation differ in several properties. As Fig. 1 shows, for equal degrees of oxidation the whiteness of the cellulose is higher in the case of activation. It is known that pectins and lignin are oxidized considerably more readily than cellulose [4], so that it is probable that activators accelerate the oxidation of the accompanying substances to a somewhat greater extent than that of cellulose itself, which results in the observed effect of increased whiteness.

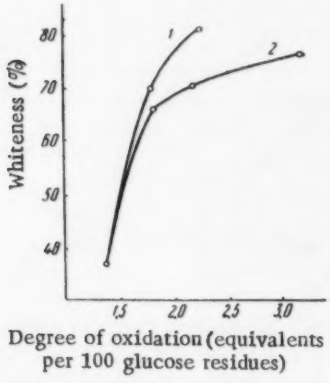

Fig. 1. Relation between whiteness and degree of oxidation for unpurified cellulose: 1) activated oxidation; 2) unactivated oxidation.

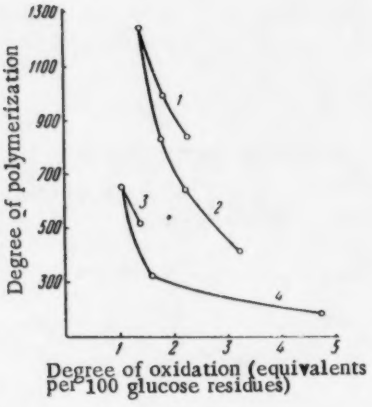

Fig. 2. Relation between degree of polymerization and degree of oxidation of cellulose: 1) unpurified cellulose, activated oxidation; 2) unpurified cellulose, unactivated oxidation; 3) purified cellulose, activated oxidation; 4) purified cellulose, unactivated oxidation.

The second peculiarity of activated oxidation is the low fall in the viscosity of cellulose in solution, as is shown in Figure 2. For a given degree of oxidation the degree of polymerization of samples that have received activated oxidation is higher than that of samples subjected to unactivated oxidation. The cause of this difference may lie in the difference in the durations of the reactions necessary for the attainment of equal chemical modification. The rates of the two processes – oxidation and hydrolysis – are different. In the course of the short activated bleach hydrolytic breakdown of cellulose at the glucosidic linkages proceeds to a less extent than during the longer period of unactivated oxidation. On the other hand, it is possible that the cause of the lower fall in degree of polymerization lies in the more rapid conversion of the carbonyl groups, which are responsible for the isomerization and breakdown of the cellulose macromolecule in an alkaline medium, into carboxyl groups, which are not so effective in the

weakening of glucosidic linkages.

Hence, in the activated oxidation on cellulose all oxidative reactions are accelerated. The difference in the final result, i.e., lower fall in degree of polymerization and higher whiteness for a given degree of oxidation, is to be explained by the different kinetic conditions of the activated and unactivated reactions and probably also by the different extents to which the reactions of oxidation of cellulose and of oxidation of the colored substances that accompany it in the fiber are accelerated.

SUMMARY

1. The chemical changes in the macromolecule of cellulose during activated oxidation with hypochlorite are the same in nature as those occurring during oxidation in absence of activators.

2. Activated oxidation is accompanied by a lower fall in degree of polymerization than unactivated oxidation.

3. It is suggested that activators accelerate the oxidation of the colored substances that accompany cellulose to a somewhat greater extent than the oxidation of the cellulose itself.

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APPLICATION OF THE KAUFMAN-GALPERN BROMOMETRIC METHOD OF DETERMINING IODINE VALUES TO SOME C_5 AND C_6 HYDROCARBONS

E. A. Timofeeva, V. M. Kleimenova, and T. P. Dobrynina

While working on the dehydrogenation of C_5 and C_6 hydrocarbons, we found it necessary to determine the unsaturation of the catalyzates. For this purpose we used the bromometric method described by Galpern [1]. As early as 1926, Kaufman [2] suggested the use of a solution of bromine in methanol saturated with sodium bromide for the determination of the unsaturation of fats. Later, Galpern and coworkers [1, 3] applied this method in the analysis of individual unsaturated hydrocarbons and cracking gasolines. The Kaufman-Galpern method now forms the basis of a standard on the determination of the iodine values of gasolines [4]. Petrov [5], working on the synthesis and catalytic transformations of unsaturated hydrocarbons, investigated the behavior of 170 hydrocarbons toward Kaufman's solution, and he concluded that for some hydrocarbons the experimental bromine values agreed with the calculated values, but for others they did not: it depended on the structure of the hydrocarbon.

In the present investigation we attempted to determine the applicability of the Kaufman-Galpern procedure to the determination of iodine values, and therefore the contents of unsaturated hydrocarbons, of catalyzates obtained by the dehydrogenation of n-pentane, isopentane, and n-hexane. The original saturated hydrocarbons, hydrocarbons formed in the catalytic process, and artificial mixtures of these hydrocarbons (corresponding approximately in composition to the catalyzates obtained) were investigated with respect to their behavior toward the bromine solution.

The solutions were prepared and the iodine values were determined in accordance with Galpern's procedure [1]. The thiosulfate was standardized against potassium dichromate. The solvent was a 1 : 1 mixture of methanol (distilled over potassium hydroxide) and cryoscopic benzene. 2-Pentene was prepared by the Grignard method from propionaldehyde and ethyl bromide; isopentenes and n-hexenes were prepared by dehydration of isopentyl and n-hexyl alcohols in presence of alumina followed by careful rectification. The properties of all the hydrocarbons investigated were closely in accord with the reported values and are therefore not given. The results are given in the table.

As was to be expected, the iodine values of n-pentane, isopentane, 2-methylpentane, cyclopentane, cyclohexane, benzene, and toluene were found to be zero. The bromination of the unsaturated hydrocarbons having one double bond proceeded almost exactly in accordance with calculation for 1 mole of bromine per 1 mole of hydrocarbon (see table). The iodine values of artificial mixtures (Mixtures no. 1, 2, 3, and 4) also closely agreed with calculated values. These results are in agreement with the conclusions of Galpern [1, 3] and Petrov [5], in spite of the fact that these workers carried out the bromination with Kaufman's solution under somewhat different conditions than those later recommended by Galpern [1] and adopted by us: they used a bromine solution of about 0.1 N concentration, and ours was about 0.2 N; Galpern used chloroform as solvent for individual unsaturated hydrocarbons, and we used a mixture of methanol and benzene.

Under the conditions of analysis, diolefins, such as piperylene, isoprene, and cyclopentadiene, are brominated to the extent of about 60%. On the basis of our results it was found to be possible to determine the monoolefin content of a mixture of monoolefins, conjugated diolefins, and alkanes (if the amount of diolefins is known) from the iodine value determined by the Kaufman-Galpern method. Calculation is made by the formula:

$$H = \frac{IM}{254} \text{ --- } 1.2D$$

in which H is the monoolefin content (% by weight), I is the iodine value, M is the molecular weight of the monoolefin, 254 is the molecular weight of iodine, D is the diolefin content (% by weight), and 1.2 is an experimental coefficient. The monoolefin contents of Mixtures no. 5 and 6 (see table) were calculated by this formula. As will be seen from the table, good results were obtained.

TABLE

Hydrocarbon	Iodine value	Content of unsaturateds (% by weight)		No.	Mixture of hydrocarbons (% by weight)	Iodine value	Monoolefin content (% by weight)	
2-Pentene	366.3	100.9	100.9	1	33.6 2-pentene and 66.4 n-pentane	122.3	33.7	33.6
	367.1	101.2				121.4	33.5	
	365.2	100.6				120.6	33.2	
						122.2	33.6	
2-Methyl-1-butene	368.9	101.6	100.8	2	34.4 2-pentene and 65.6 n-pentane	124.7	34.4	34.3
	364.6	100.5				124.5	34.3	
	367.7	100.3				124.1	34.2	
	366.4	101.0	100.6	3	52.0 isopentenes and 48.0 isopentane	187.9	51.8	51.9
	363.9	100.3				188.9	52.1	
2-Methyl-2-butene	362.1	99.8	99.5			190.4	52.4	52.2
	360.1	99.2				188.6	52.0	
3-Methyl-1-butene	359.4	99.1	99.9	4	9.4 hexenes (63.0-68.0°) and 90.6 n-hexane	29.5	9.7	9.5
	364.8	100.8				28.2	9.3	
						28.9	9.5	
n-Hexenes (63.0-67.0°)	304.3	100.6	100.5	5	41.0 isopentenes, 8.0 isoprene, and 51.0 isopentane	186.8	41.8	41.5
	303.6	100.4				183.6	41.0	
						186.8	41.8	
n-Hexenes (67.0-68.0°)	300.9	99.5	100.0			182.5	40.7	40.8
	303.6	100.4				183.0	40.8	
Piperylene	486.9	65.2	65.4	6	32.6 2-pentene, 6.5 piperylene, and 60.9 n-pentane	147.7	32.9	33.0
	490.6	65.7				148.2	33.0	
						148.5	33.1	
Isoprene	443.7	59.4	59.7					
	448.8	60.1						
	442.2	59.2	59.4					
	444.6	59.5						
Cyclopentadiene	432.6	56.2	55.1					
	420.9	54.7						
	421.4	54.7						

SUMMARY

1. It was shown that, in its application to individual C_5 and C_6 monoolefins and their mixtures with alkanes, the Kaufman-Galpern bromometric method of determing iodine values gives good results.

2. A coefficient was found with aid of which it was found possible to determine the content of monoolefins in their mixtures with conjugated diolefins and alkanes by the bromometric method of Kaufman and Galpern.

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RAMAN SPECTRA OF ORGANOSILICON, ORGANOGERMANIUM, AND ORGANOTIN COMPOUNDS CONTAINING ALLYL GROUPS

Yu. P. Egorov

Study of the Raman spectra of allylsilanes ($R_3Si - CH_2CH = CH_2$) [1, 2] showed that the positions and intensities of the Raman lines of the $-CH_2CH = CH_2$ group are independent of the identity of R. It was of interest to examine the way in which these frequencies are affected by replacement of Si by a metal of group IV, namely Ge or Sn. Raman spectra of organogermanium and organotin compounds containing unsaturated groups have not been reported in the literature.

We determined the spectra of $(CH_3)_3Ge - CH_2CH = CH_2$ (II) and $(CH_3)_3SnCH_2CH = CH_2$ (III), which were synthesized as described in the paper [3]. Below we give the frequencies found (cm^{-1}; intensities expressed on a visual scale).

$(CH_3)_3GeCH_2CH = CH_2$ – 183(5 b), 198(5 b), 263(2), 400(3 b), 526(6), 572(10), 600(6), 688(3), 759(1), 806(0), 890(2), 930(1), 990(1), 1144(5), 1195(3), 1243(4), 1300(3), 1398(3), 1420(2), 1630(4 sh), 2852(2), 2909(8 b), 2935(3), 2973(5), 2994(4), 3080(3).

$(CH_3)_3SnCH_2CH = CH_2$ – 162(4), 230(0 b), 335(0), 396(3 b), 424(1), 457(2), 482(4 b), 510(10), 532(6), 671(2), 882(1), 930(1), 991(1), 1095(5 b), 1145(1), 1192(5 db), 1298(3), 1335(1), 1375(0), 1398(2), 1420(1), 1625(4 sh), 2912(3 b), 2988(3 b), 3082(2).

The characteristic frequencies of the group $- CH_2CH = CH_2$, as compared with its frequencies in $(CH_3)_3SiCH_2CH = CH_2$ (I) are given in the table.

TABLE

Characteristic Frequencies of $CH_2 = CH - CH_2 - X$ Groups

$(CH_3)_3SiCH_2$ $CH=CH_2$ (I)	$(CH_3)_3GeCH_2$ $CH=CH_2$ (II)	$(CH_3)_3SnCH_2$ $CH=CH_2$ (III)
410	400	396
896	890	880
930	930	930
990	990	990
1155	1140	1095
1193	1195	1192
1300	1300	1298
1398	1398	1398
1630	1630	1625
3000	2994	2988
3080	3080	3080

It can be seen that a series of frequencies – 930, 990, 1193, 1300, 1398, and 3080 cm^{-1} remain constant as we pass from (I) to (III); the C = C frequency at 1630 cm^{-1} also changes little [by – 5 cm^{-1} in (III)]. It may therefore be supposed that all these frequencies are associated with vibrations of the final $- CH = CH_2$ group, which is fairly far removed from the metal atom. The progressive lowering of the symmetrical frequency of the C – H of CH_2 – 3000 in (I), 2994 in (II), and 2988 in (III) – is somewhat unexpected. There is a considerable lowering in the frequency of the intense line at 1155 cm^{-1} [1140 in (II) and 1095 in (III)], which is found in all compounds known to us which have a double bond in the β-position to Si. It is possible that this frequency is associated with the valence vibration of C – C, raised (it is usually about 1000 cm^{-1}) owing to conjugation of Si – C and C = C bonds [4] (cf. butadiene – 1200 cm^{-1}).

In conclusion, we will point out the positions of the valence vibrations of the skeleton. In tetramethyl derivatives these frequencies are: for Si $(CH_3)_4$, 595 and 695; for Ge $(CH_3)_4$, 558 and 595; for Sn $(CH_3)_4$,

507 and 532 cm^{-1} [5,6]. There is a progressive lowering of both frequencies [the first is completely symmetrical (A), and the second is threefold degenerate (F_2)] and they approach one another. In the compounds (I), (II), and (III) three intense lines are found in this region, which corresponds to approximate symmetry of the skeleton C_{3v}; they are: (I) – 556, 630, 695; (II) – 526, 572, 600; (III) – 482, 510, 532 cm^{-1}. The way in which the positions of these frequencies change is the same as for the tetrasubstituted compounds. The position of the last of these frequencies is noteworthy – its position is not affected by replacement of one of the CH_3 groups by $-CH_2CH=CH_2$.

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LETTER TO THE EDITOR

Sir:

As is well known, differential heats of adsorption Q can be measured calorimetrically or can be calculated thermodynamically from adsorption isosteres by the Clausius-Clapeyron Equation, $d \log p / d(T^{-1}) = -Q/R$ (1). It is known also that, in spite of its controversial theoretical basis, the fundamental postulate of the potential theory of adsorption is often found to be valid, i.e., at a given value of aV, the adsorption potential $\epsilon = -RT \log h$ is independent of temperature ($h = p/p_s$, a = adsorption, V = molar volume). This postulate is equivalent to the condition $(daV/dT)_\epsilon = 0$ (2).

The object of this letter is to show that, by a rigorous thermodynamic procedure, an equation can be derived from the condition (2) which enables us to calculate $Q = Q(a)$ from a single adsorption isotherm. In fact, according to the choice of variables, the thermal adsorption equation can be written in the following forms: $f(aV, T, T \log h) = 0$ (2) $F(aV, T \log h) = 0$ (4); $\varphi(a, T, \log h) = 0$ (5). From equations (3) and (2) we obtain the relationship $(d \log h / dT)_{aV} = -\log h / T$ (6), and from (4) and (6) it follows that $(da/dT)_{\log h} = [(da/d \log h)_T \log h / T] - \alpha a$ (7), in which α is the coefficient of cubic expansion of the adsorbate. Finally, from (1), (5), and (7) we obtain the equation:

$$Q - \lambda = q = \alpha RT^2 (d \log h / d \log a)_T - RT \log h, \qquad (8)$$

in which q is the so-called pure heat of adsorption, and λ is the latent heat of evaporation. We must point out that, although all the above is contained in Polanyi's theory, the expression (8) has not been given in this form and has not been applied to the calculation of Q(a). Verification of the equation (8) for a large amount of published data showed that the discrepancy between calculated and experimental values of Q does not exceed 5-7%.

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CURRENT EVENTS

SESSION OF THE INTERNATIONAL COMMISSION ON THE NOMENCLATURE OF ORGANIC COMPOUNDS

A Session of the International Commission on the Nomenclature of Organic Compounds was held in Copenhagen from August 27 to September 1, 1956. The Academy of Sciences of the USSR detailed A. P. Terentyev, Corresponding Member of the Academy, and V. M. Potapov, Cand. Chem. Sci. to attend; the former was an official participant of the Session of the Commission in the capacity of an observer.

In the course of the summer of 1956, the Nomenclature Commission of the Division of Chemical Sciences of the Academy of Sciences of the USSR studied numerous documents and proposals sent from the International Commission. For their part, members of the Soviet Commission sent the International Commission both previously published material * and also new proposals on the matters to be discussed at Copenhagen. These documents were in English and were given to all members of the International Commission.

The composition of the International Commission was as follows: P. E. Verkade (Holland) - chairman; S. Veibel (Denmark) - vice-chairman; G. Nutting (USA) - secretary; G. M. Dyson (Britain) - secretary; R. S. Cahn (Britain); A. D. Mitchell (Britain); L. T. Capell (USA); J. Kersen (France); N. Lozac'h (France); F. Richter (German Federal Republic); and as observers: A. P. Terentyev (USSR) and Jensen (Denmark) – from the International Commission on the Nomenclature of Inorganic Compounds.

The Commission worked very intensively from 9 a.m. to 7 p.m. every day, i.e 7-8 hours with a break for lunch. Also, the participants generally met and conversed unofficially in the evenings and during Sunday walks. This enabled us to acquaint ourselves more closely with the work of the Commission and the personal views of its members.

Although we presented our proposals to the Commission, we did not have much hope of exerting a substantial effect on the course of its work. The work of the International Commission was based on the so-called Liege rules of nomenclature of 1930, and the Commission, operating with the same members, has worked on the review and supplementation of this for several years. The main new proposals were presented by the Editorial Board of Chemical Abstracts; they reflected the present practice of this journal and took no account of the possibility of their international applicability. All the material of the Commission was presented only in English, and all discussions were carried out only in English. It is not surprising, therefore, that the rules of nomenclature proposed by the International Commission are most satisfactory in fulfilling the needs of abstracting in the English language.

Most attention was devoted to the examination of the nomenclature of compounds containing functions and functional derivatives with mono-, poly-, and hetero-functions. General questions were not discussed. The Commission concerned itself only with putting a certain degree of order into various forms of naming. One long-standing member of the Commission aptly described this sort of work as "the collection of chemical folklore." The Commission intends to turn its attention to radical review of the chaos of nomenclature only when the first stage is complete -- in 3-5 years time.

In taking part in work of this sort, we could introduce only a few, though fairly significant, corrections, these being of importance in connection with the system of nomenclature accepted by the Nomenclature Commission of the Division of Chemical Sciences. Thus, proposals of the Editorial Board of Chemical Abstracts

* A. P. Terentiev, A. N. Kost, A. M. Zuckerman, V. M. Potapov, Vorschläge zur Nomenklatur organischer Verbindungen, INI AN SSSR Press, Moscow, 1955.

require alphabetical order for the arrangement and seniority of functional groups in the English language, whereas the plan that we introduced recommended a logical order based on the generally accepted systematics of organic compounds. This proposal was staunchly supported by F. Richter, chief editor of Beilstein's Handbuch. As the result of discussion, the International Commission accepted the proposal of the Editorial Board of Chemical Abstracts for the English language; it was proposed that F. Richter and A. P. Terentyev should work out systematic rules for the Russian and German languages.

On the question of the nomenclature of compounds containing labeled atoms, in the main our proposals were accepted. On our suggestion, the International Commission accepted the term "atsid" for use in the Russian language for acidic functions.

Many points in the extensive agenda of the Session were scarcely touched, or were not considered at all.

When the Session had closed, an unofficial meeting was held at which V. M. Potapov, a member of the Nomenclature Commission of the Division of Chemical Sciences of the Academy of Sciences of the USSR, gave a report on the work of our Commission and of the Institute of Scientific Information on chemical nomenclature and on the basic principles of the system of organic nomenclature that we have developed. The paper was followed by a lively exchange of views.

In summarizing the results of the Session, we must again emphasize that, in their work, the members of the International Commission are using and seriously considering only the norms of nomenclature that have been developed and established in existing practice without waiting for their examination and approval by the International Commission.

The next session of the Commission will be in Paris in July, 1957.

A. P. Terentyev
V. M. Potapov

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Division of Chemical Sciences

IN ENGLISH TRANSLATION

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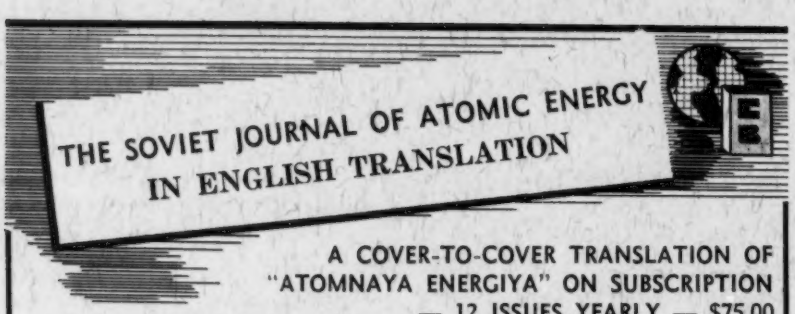

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